THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Chemical substitution with a life cycle perspective

The case of per- and polyfluoroalkyl substances in durable water repellents

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ERRATA

p. III – …what messages can motivate consumers **towards** voluntary substitution.

p. 4 – The PFAAs **degrade slowly in air and negligibly in other media (Cousins et al., 2019)**, and their emissions...

p. 20 – (one reason being to capture potential impacts of persistent and mobile chemicals such as **certain** PFASs)

p. 20 – the USEtox characterisation factors have the following units: midpoint human health characterisation factor [cases/$kg_{emitted}$], midpoint ecotox. charact. factor [$PAF.m^3.d/kg_{emitted}$]

p. 30 – The LCA referred to was conducted on a lightweight shell jacket, cradle-to-grave

p. 46 – Experiences from the studies associated to the phase-out of **certain hazardous** PFASs from DWR applications…

p. 48 – …where test results on **e.g.** life length…

p. 51 – Alternative DWRs were indicated to differ substantially in **toxicity** performance compared to side-chain fluorinated polymer based C8 DWRs…

REFERENCES

COUSINS, I. T., NG, C. A., WANG, Z. & SCHERINGER, M. 2019. Why is high persistence alone a major cause of concern? *Environ Sci Process Impacts,* 21**,** 781-792.

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ABSTRACT

The aim of the research presented in this thesis was to support the process of substitution of side-chain fluorinated polymers in durable water repellents (DWRs), that give rise to emissions of hazardous per- and polyfluoroalkyl substances (PFASs). The focus was on: *i)* the provision of improved decision support regarding the environmental and human health performance of alternatives, and *ii)* public readiness for substitution and what messages can motivate consumers to voluntary substitution.

This research explored the applicability of life cycle assessment (LCA) for the provision of a life cycle perspective in chemical alternatives assessment (CAA). To improve the relevance of LCA in the CAA of DWR alternatives, contributions were made to the life cycle impact assessment (LCIA) of (eco)toxicity, and characterisation factors were calculated (Papers II and III). Case study results (Paper IV), together with a literature review (Paper V), showed that LCA can provide relevant information for CAAs. Potential problem-shifting was identified between DWR alternatives, and the scenario assessment in the LCA provided useful input to the CAA. The hazard assessment (Paper I) together with the LCA support the recommendation to phase-out all non-essential use of PFASs in DWR.

Performing such a phase-out through regulation can be a slow process. The potential to accelerate a phase-out by motivating consumers to voluntary substitution was investigated using a web-survey experiment. This study (Paper VI) found that Swedish readiness to voluntarily act to substitute hazardous fluorinated chemicals is already high and that detailed information on the hazards associated with these chemicals can raise this potential even higher.

The present research strengthens the potential for LCA to be used in CAA and identifies its limitations. The work will help policy makers and analysts who are faced with challenges such as prioritising regulatory and design interventions for substitution and shaping information campaigns to encourage voluntary substitution.

Key words: LCA, LCIA, DWR, PFAS, CAA

LIST OF PUBLICATIONS

The thesis is based on the following papers, referred to by roman numerals in the introductory chapters (*i.e.* in the Kappa).

I. Holmquist, H.*, Schellenberger, S.*, van der Veen, I., Peters, G. M., Leonards, P. E. and Cousins, I. T., (2016). "Properties, performance and associated hazards of state-of-the-art durable water repellent (DWR) chemistry for textile finishing." *Environment International* 91: 251-264. DOI: https://doi.org/10.1016/j.envint.2016.02.035

II. Roos, S., Holmquist, H., Jönsson, C. and Arvidsson, R. (2018). "USEtox characterisation factors for textile chemicals based on a transparent data source selection strategy." *The International Journal of Life Cycle Assessment* 23(4): 890-903. DOI: https://doi.org/10.1007/s11367-017-1330-y

III. Holmquist, H., Fantke, P., Cousins, I.T., Owsianiak, M., Liagkouridis I. and Peters G.M. (2020). "An (eco)toxicity life cycle impact assessment framework for per- and polyfluoroalkyl substances" *Environmental Science and Technology.* DOI: http://dx.doi.org/10.1021/acs.est.9b07774).

IV. Holmquist, H., Roos, S., Schellenberger, S., Jönsson, C. and Peters G.M. (2020) Life cycle assessment to support substitution of hazardous highly fluorinated chemicals in durable water repellents on outdoor garments (Manuscript)

V. Harder, R., Holmquist, H., Molander, S., Svanström, M. and Peters, G. M. (2015). "Review of Environmental Assessment Case Studies Blending Elements of Risk Assessment and Life Cycle Assessment." *Environmental Science & Technology* 49(22): 13083-13093. DOI: https://doi.org/10.1021/acs.est.5b03302

VI. Holmquist, H., Jagers, S.C., Matti, S., Svanström, M. and Peters, G.M. (2018). "How information about hazardous fluorinated substances increases willingness-to-pay for alternative outdoor garments: A Swedish survey experiment." *Journal of Cleaner Production* 202: 130-138. DOI: https://doi.org/10.1016/j.jclepro.2018.07.215

* Shared first authorship

Work related to the thesis has also been presented in the following publications:

A. Andersson[#], H., Harder, R., Peters, G.M. and Cousins I.T. (2014). SUPFES: Environmental risk assessment on short-chain per- and polyfluoroalkyl substances applied to land in municipal sewage sludge. Poster at the 6th INTERNATIONAL WORKSHOP on Per- and Polyfluorinated Alkyl Substances – PFASs, Idstein, Germany.

B. Holmquist, H., Lexén, J., Rahmberg, M., Sahlin, U., Grönholdt Palm, J. and Rydberg, T. (2018). "The potential to use QSAR to populate ecotoxicity characterisation factors for simplified LCIA and chemical prioritisation." *International Journal of Life Cycle Assessment* 23(11): 2208-2216. DOI: https://doi.org/10.1007/s11367-018-1452-x

C. Fantke, P., Aurisano, N., Bare, J., Backhaus, T., Bulle, C., Chapman, P. M., De Zwart, D., Dwyer, R., Ernstoff, A., Golsteijn, L., Holmquist, H., Jolliet, O., McKone, T. E., Owsianiak, M., Peijnenburg, W., Posthuma, L., Roos, S., Saouter, E., Schowanek, D., van Straalen, N. M., Vijver, M. G. and Hauschild, M. (2018). "Toward harmonizing ecotoxicity characterization in life cycle impact assessment." *Environmental Toxicology and Chemistry* 37(12): 2955-2971. DOI: https://doi.org/10.1002/etc.4261

D. Heimersson, S., Holmquist, H., Svanström, M., Molander, S. and Peters, G.M. (2019) How uncertainties are handled in LCA – focus on the wastewater and textile sectors. Oral presentation/abstract. Watermatex September 1- 4 2019, Copenhagen.

My maiden name

Contribution report

The author of this thesis has made the following contributions to the papers:

I. Shared first authorship with Steffen Schellenberger (Stockholm University). Developed the idea of the study together with the co-authors. Performed the research and wrote the corresponding text for the hazard assessment parts of the article. Wrote large parts of the abstract, introduction, and discussion. Developed Figs. 2 and 3 together with Steffen Schellenberger. Made adjustments based on feedback and contributions from all co-authors and reviewers.

II. Developed the data collection strategy together with Sandra Roos (Chalmers/RISE). Performed the research and wrote the corresponding text for the data estimation procedures. Evaluated the results and developed recommendations together with Sandra Roos. Provided feedback, together with co-authors, on the full text throughout the publication process.

III. Developed the research design, conducted the data collection and modelling, and wrote the text. Feedback from the co-authors was given in all parts of the work.

IV. Developed the research design together with the co-authors. Conducted the data collection and modelling and wrote the text. Feedback from the co-authors was given in all parts of the work.

V. Contributed to analysis and discussion of the reviewed literature and the conclusions drawn, as well as the structure of the article. Robin Harder (Chalmers) conducted the literature review and wrote major parts of the text.

VI. Developed the research design together with the co-authors. Conducted the statistical analysis and wrote the text. Feedback from the co-authors was given in all parts of the work.

Abbreviations

BPA	Bisphenol A
BPS	Bisphenol S
C4, C6, C8	The number of carbon atoms in the perfluorinated alkyl side-chain of the polymer (see further p. 7)
CAA	Chemical Alternatives Assessment
CF	Characterisation Factor
CRA	Chemical Risk Assessment
D4	Octamethylcyclotetrasiloxane
D5	Decamethylcyclopentasiloxane
DMSD	Dimethylsilanediol
DOC	Dissolved Organic Carbon
DWR	Durable Water Repellent
ECHA	European Chemicals Agency
EF	Effect Factor
EFSA	European Food Safety Authority
EPD	Environmental Product Declaration
FF	Fate Factor
FTA	Fluorotelomer Acrylate
FTOH	Fluorotelomer Alcohol
iF	Intake Fraction
KOW	Octanol-Water Partitioning Coefficient
LCA	Life Cycle Assessment
LCC	Life Cycle Costing
LCIA	Life Cycle Impact Assessment
MDQ	Minimum Data Quality
NEP	New Environmental Paradigm
NGO	Non-Governmental Organisation
OECD	Organisation for Economic Co-operation and Development
OPFR	Organophosphate Ester Flame Retardants
PASF	Perfluoroalkane Sulfonyl Fluorides
PBDE	Polybrominated Diphenyl Ethers
PBT	Persistent and Bioaccumulative and Toxic
PEF	Product Environmental Footprint
PFAA	Perfluroalkyl Acids
PFAS	Per- and Polyfluoroalkyl Substances
PFBS	Perfluorobutane Sulfonic Acid
PFCA	Perfluorinated Carboxylic Acid

PFHxA	Perfluorohexanoic Acid
PFOA	Perfluorooctanoic Acid
PFOS	Perfluorooctanesulfonic Acid
PFSA	Perfluorinated Sulfonic Acid
PM	Persistent and Mobile
POP	Persistent Organic Pollutants
REACH	Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals
S-LCA	Social Life Cycle Assessment
SUPFES	Project: Substitution in Practice of Prioritized Fluorinated Chemicals to Eliminate Diffuse Sources
SVHC	Substance of Very High Concern
TMS	Trimethylsilanol
UNEP	United Nations Environment Programme
VBN	Value Belief Norm
vPvB	very Persistent and very Bioaccumulative
vPvM	very Persistent and very Mobile
XF	Exposure Factor

Contents

1 Introduction

1.1 Managing chemical risks

Modern society is dependent on a large number of chemicals (see *e.g.* UNEP (2012)), and humans and the environment are constantly being exposed to chemical risks; in our workplaces, by consumer products, and via environmental exposure. There are regulations in place, especially in the developed world, to ameliorate those risks (*e.g.* REACH; Registration, Evaluation, Authorisation and Restriction of Chemicals, Regulation (EC) No 1907/2006), but given the wickedness of the problem (the many chemicals and the problem's extension across environmental media, borders, and jurisdictions) complete safety by regulation is difficult (Allen, 2013). Chemical risks cannot be completely contained as long as hazardous chemicals are in use (Kaplan and Garrick, 1981), and as the ending of such use is not foreseeable, it is imperative that chemical risk management is based on sound priorities. The assessment on which such management is based must be sufficiently comprehensive for it to support sustainable development where neither the current generation nor future generations are put at risk of an unhealthy environment.

No risk is acceptable unless it comes with a benefit (Kaplan and Garrick, 1981). Thus, risk management must be adjusted so that there is an acceptable trade-off for all exposed to the hazard, *i.e.* all at risk (Fischhoff, 1995). The use of chemicals clearly comes with a benefit for the user of the products (and for the producer who earns from chemicals manufacture). The user of the product may very well perceive the risks as acceptable, as the benefits are large and the risks seem small, either because they are not completely understood or because they are not relevant for the user but might be for someone else. The risks connected to this chemical use may occur elsewhere than where the end-product is used, both geographically and in time, and hence, a life cycle perspective is relevant. Hansson (2018) identifies three major stakeholder roles: risk-exposed, decision makers (about the risk), and beneficiaries, and argues that ethical risk assessment should be disaggregated to consider all three roles. Problematic cases were identified to be those where the beneficiary and the decision maker are the same actor, and when the risk-exposed is neither decision maker nor beneficiary. An ethical assessment of risk must consider both the risk-exposed and the beneficiaries.

1.1.1 The life cycle perspective

A life cycle perspective implies that not only are the consequences of an action for the beneficiary considered relevant, but also consequences for others and possibly also consequences in the future (if possible to predict): cradle-to-grave. In a chemical risk context, it is the life cycle of a chemical[1] of concern that can be relevant, *i.e.* its synthetic history, use phase emissions, and waste handling, but also other emissions and resource outtake related to the product or service under study are relevant. Hence, a life cycle perspective can be applied to identify (and avoid) sub-optimisation in product design, *e.g.* avoid problem-shifting by moving risk from one type of chemical emission to another or to another impact category. Substitution of lead solders can serve as one example of this: increased air pollution was identified as a consequence of the substitution of lead solders with tin/silver/copper solders as the latter require higher energy use (Lofstedt, 2014). LCA is one tool that incorporates the life cycle perspective and makes it possible to compare the potential impacts of a range of impact categories, including ecotoxicity and human toxicity (hereafter (eco)toxicity), between products (or services) and within the life cycle of a product.

1.1.2 Chemical substitution

Hansson *et al.* (2011) describe substitution to be '…replacement of hazardous (or potentially hazardous) chemical substances by less hazardous alternatives', which is the definition applied herein. Substitution can be intended to retain identical functionality with the use of a 'drop-in chemical' very similar to the original substance (Tickner *et al.*, 2015). It can, however, be the case that the similar chemical results in similar problems, *i.e.* 'regrettable substitution' (see e.g. Fantke *et al.*, 2015, Harremoës *et al.*, 2001, Bergman *et al.*, 2012, Rochester and Bolden, 2015, Tickner *et al.*, 2019b). Examples are many, *e.g.* the substitution of bisphenol A (BPA) with bisphenol S (BPS), also associated with hazardous properties of concern (Zimmerman and Anastas, 2015), or the substitution of polybrominated diphenyl ethers (PBDEs) with organophosphate ester flame retardants (OPFRs) (Blum *et al.*, 2019). To avoid the introduction of other hazardous chemicals, it has been argued that substitution should be fundamental rather than incremental, *i.e.* introduce fundamentally different molecular structures as alternative chemicals (Fantke *et al.*, 2015). In line with such thoughts, focus should be on the function of the end-product rather than on the chemical (Tickner *et al.*, 2015, Geiser *et al.*, 2015, Fantke and Illner, 2019), which would allow for not only fundamentally different molecules but also different product designs. Chemical alternative assessment (CAA), for prioritising alternatives (chemical

[1] The term 'life cycle of a chemical' can have other meanings in other contexts, *e.g.* with regards to innovation developments, but those are not considered further here.

and non-chemical) to the chemical of concern, is key to achieving a successful substitution (Geiser *et al.*, 2015).

There are frameworks available to support CAA (Jacobs *et al.*, 2016). The central components in those frameworks are hazard, technical feasibility, and economic viability assessments. Life cycle thinking or life cycle analysis (LCA) to avoid problem-shifting is often recommended, but the lack of standardisation of the former and the data shortage for the latter have been identified as major challenges (Jacobs *et al.*, 2016, Tickner *et al.*, 2019a, Oguzcan *et al.*, 2019). Moving from incremental to fundamental (or even product-function-based) substitution to avoid the introduction of new hazardous chemicals, problem-shifting will become more likely than before as both the chemical life cycle and the product life cycle of the alternatives will differ from those of the original product. Hence, successful substitution depends on a CAA with comprehensive life cycle considerations that identify problem-shifting, and cover the relevant potential impacts as well as relevant product life cycle stages.

After CAA has been performed, chemical substitution can be enforced by legislation placing restrictions or complete bans on chemicals (*e.g.* REACH and Stockholm Convention on persistent organic pollutants (POPs)). Substitution can also be enforced by voluntary actions by companies or trade organisations (Scruggs, 2013), or by the public either as consumers or part of social movement actions (Lissner and Romano, 2011, Tickner *et al.*, 2019b, Cousins *et al.*, 2019a). Legislative action can be a slow process that takes many years, especially if the scope has a broad geographical area (see *e.g.* the REACH restriction process (ECHA, 2020b) or a substitution process as described by Lofstedt (2014)). Voluntary actions have potential to be faster if the public is engaged in the issue (Wickman *et al.*, 2009, Micheletti, 2003).

1.2 The case of per- and polyfluoroalkyl substances in durable water repellents

1.2.1 This research in its substitution context

Durable water repellents (DWRs) are applied to textiles to achieve water repellency. The water repellency of the outer textile is desirable in apparel and footwear made of breathable materials. The textile often has a membrane or coating on the inside that makes it impermeable to water droplets, and subsequently, the DWR function is to prevent the outer textile from becoming soaked in water, which would make it heavy and cold when used in rain. DWRs can also provide repellency for other liquids, giving the textile additional functions that provide safety in environments with hazardous liquids (Schellenberger *et al.*, 2019a). Repellency towards oil and/or other liquids can also reduce washing needs. Per- and polyfluoroalkyl

substances (PFASs) in the form of side-chain fluorinated polymers are excellent DWRs as they are durable and provide water as well as oil repellency (Schellenberger *et al.*, 2019a, Schellenberger *et al.*, 2018). However, as several PFASs have been identified as hazardous to human health and the environment and are being phased-out or restricted (Cousins *et al.*, 2019a, Zushi *et al.*, 2012, Wang *et al.*, 2017, and further below), the apparel and footwear industries must find alternatives with improved environmental and human health characteristics while maintaining sufficient function.

This thesis was produced as part of an international project, Substitution in Practice of Prioritized Fluorinated Chemicals to Eliminate Diffuse Sources (SUPFES; www.supfes.eu). In the SUPFES project, DWRs were identified as interesting case study examples to test theoretical ideas about substitution. The case is further described in the licentiate thesis that this doctoral thesis followed: Holmquist (2016). The focus of this thesis has been on environmental and human health considerations, while other parts of the SUPFES project have focussed on technical performance and diffuse emissions (Schellenberger, 2019, van der Veen *et al.*, 2020, Jönsson *et al.*, 2018, Schellenberger *et al.*, 2019b, Schellenberger *et al.*, 2019a, Schellenberger *et al.*, 2018, Schellenberger, 2016, van der Veen *et al.*, 2016). The substitution process in industry has been on-going in parallel with the research conducted as part of this thesis and in the SUPFES project, and it is still on-going as industry actors are seeking alternatives with improved environmental and human health performance and acceptable chemical risks, while retaining (sufficient) function (Cousins *et al.*, 2019a).

1.2.2 Per- and polyfluoroalkyl substances

PFASs make up a large group of chemicals (>4000, OECD (2018)) with diverse properties. Buck *et al.* (2011) define PFASs as: '…aliphatic substances containing one or more C atoms on which all the H substituents present in the nonfluorinated analogues from which they are notionally derived have been replaced by F atoms, in such a manner that PFASs contain the perfluoroalkyl moiety C_nF_{2n+1}–'. The carbon-fluorine bond is very strong, and the perfluoroalkyl part of the molecule is extremely persistent. Thus, PFASs are either stable, or ultimately transform into very persistent terminal degradation products, usually perfluroalkyl acids (PFAAs) or perfluoroalkyl(poly)ether acids (Wang *et al.*, 2017). PFASs in DWRs are commonly side-chain fluorinated polymers and thus, in this thesis, the focus is not on fluoropolymers or perfluoropolyethers. PFAS degradation patterns are diverse and differ between precursors and environmental media (Butt *et al.*, 2014, Liu and Mejia Avendano, 2013). In addition, van der Veen *et al.* (2020) have shown empirically that weathering and abrasion change congener profiles of PFASs on textiles, *i.e.* before emission to the environment has occurred. The PFAAs have no natural degradation

pathways and their emissions, whether by direct emission or by precursor degradation (see an example of emission pathways relevant for PFASs on textile in Figure 1), generate increasing exposures to human and wildlife due to environmental accumulation. In addition to the persistence of degradation products, the evaluation of environmental and human health consequences of PFASs use and emissions is complicated by the amphiphilicity of the PFAAs, *i.e.* they are not fat-soluble as the original POPs (Jones *et al.*, 2003). Furthermore, PFASs can have diverse (eco)toxicological effects, such as hepatotoxicity, endocrine, immunological, and reprotoxic effects, not necessarily detected with standardised test methods (Wang *et al.*, 2017, DeWitt, 2015).

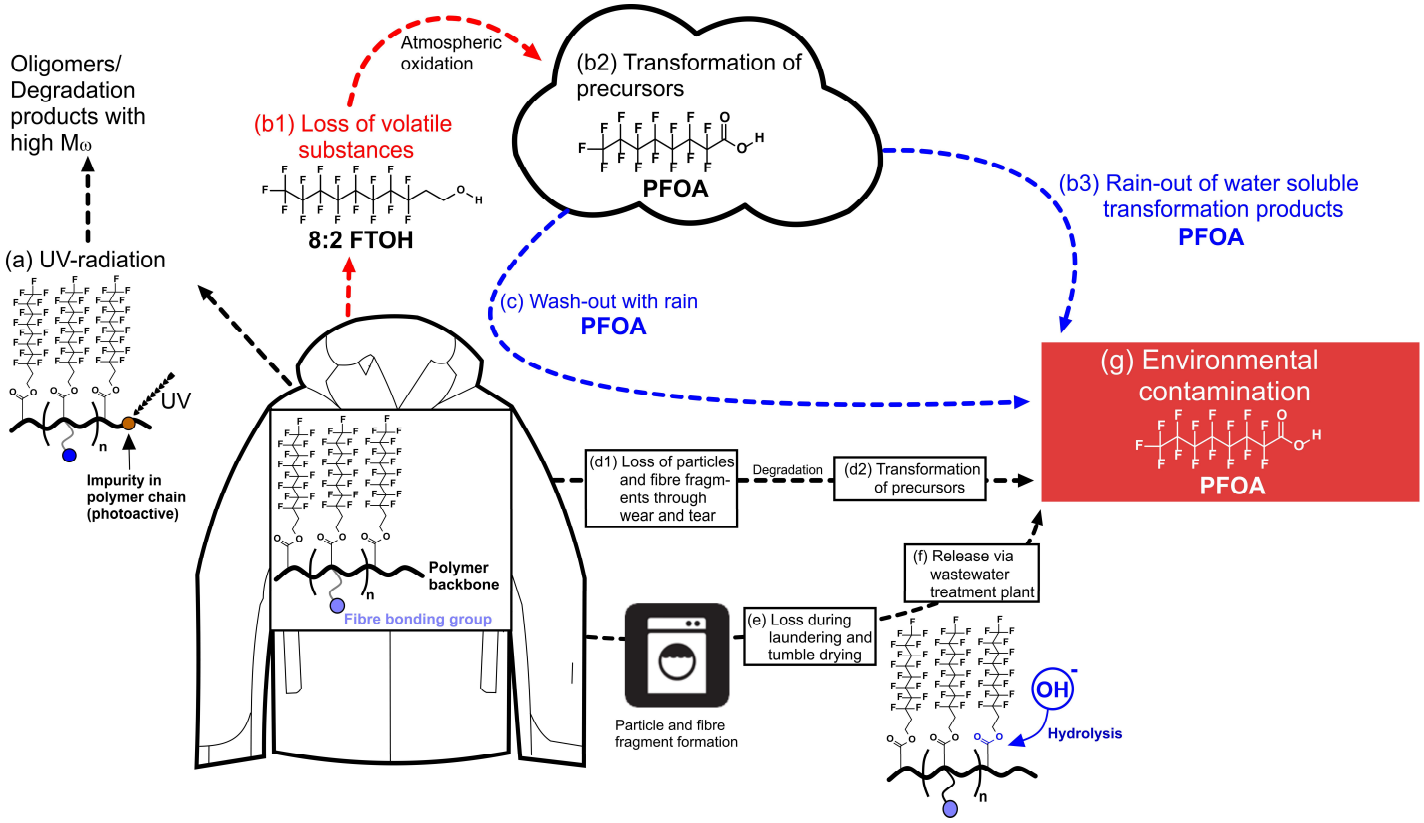

Figure 1: Simplified description of possible loss pathways of (g) perfluorooctanoic acid (PFOA) from C8 DWR-treated fabrics during the use phase. (a) Cleavage of the polymer backbone by UV-light into oligomeric/polymers, (b1) the evaporation of the 8:2 fluorotelomer alcohol (FTOH), a manufacturing residual, from the fabric; (b2) the transformation of 8:2 FTOH in the atmosphere into PFOA, (b3) the rain-out of water soluble PFOA from the atmosphere; (c) the wash-out of water-soluble residuals such as PFOA or water-soluble monomers from the garment; (d1) the loss of particles and fibre fragments containing the C8 side-chain fluorinated polymer based DWR treatment, caused by abrasion, which might undergo further degradation processes (d2) in the environment; (e) the hydrolysis of the C8-side chain during laundering, and the loss of DWR-coated fibre fragments during the washing process into the effluent; (f) the release of DWR-coated fibre fragments via a wastewater treatment plant and further transformations of these precursors in PFOA. This is Figure S7 in Paper I.

PFAAs have been divided into two groups: short- and long-chain PFAAs. Long-chain PFAAs have been defined as having an alkyl chain containing six or more carbon atoms for perfluorinated sulfonic acids (PFSAs; $C_nF_{2n+1}SO_3H$, $n \geq 6$) and seven or more carbons for perfluorinated carboxylic acids (PFCAs; $C_nF_{2n+1}COOH$, $n \geq 7$) (Buck *et al.*, 2011). Many long-chain PFAAs are covered by regulations, *e.g.* perfluorooctanoic acid (PFOA, Figure 2) and perfluorooctanesulfonic acid (PFOS) that are persistent organic pollutants (POPs) under the Stockholm Convention (decision SC-4/17, SC-9/12), and have global restrictions on production and use. As the short-chain PFAAs do not bioaccumulate, they do not qualify as POPs and have long been regarded as an environmentally benign alternative, but this is currently being re-evaluated. Perfluorobutane sulfonic acid (PFBS, Figure 2), has been identified as a substance of very high concern (SVHC), and Perfluorohexanoic acid (PFHxA, Figure 2) has been proposed for restrictions under REACH, and very persistent and very mobile (vPvM) characteristics together with the possibility of toxicity are key identifiers of both substances (ECHA, 2019a, b).

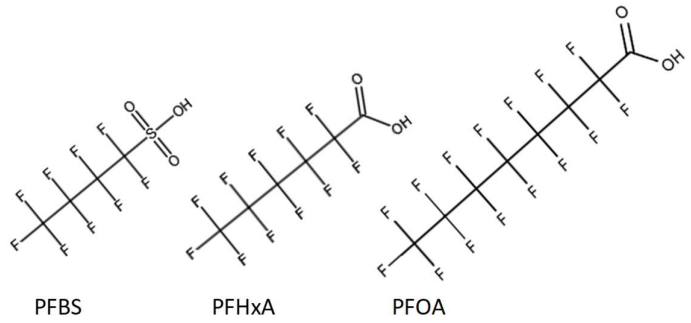

Figure 2: Chemical structures of perfluorobutane sulfonic acid (PFBS), perfluorohexanoic acid (PFHxA), and perfluorooctanoic acid (PFOA)

PFAS products based on side-chain fluorinated polymers are often denoted by the length of the perfluorinated alkyl group, *i.e.* C4, C6, and C8. It is important to note that degradation products do not necessarily have the same number of perfluorinated carbon atoms as their precursors. For example, PFOA has seven perfluorinated carbons (and is sometimes referred to as C7), but it is one of the main degradation products from a C8 system based on a 8:2 fluorotelomer acrylate (FTA) where *e.g.* 8:2 fluorotelomer alcohols (FTOHs), with eight perfluorinated carbon atoms, are transformed (see Figure 1). In this thesis, the DWR systems with side-chain fluorinated polymers are denoted C4, C6, and C8, which refers to the number of carbon atoms in the perfluorinated alkyl side-chain of the polymer. PFAAs and other non-polymeric PFASs are denoted by their chemical name.

1.3 Thesis objectives

The overall aim of the research presented herein was to support stakeholders, such as industrial actors and policy makers, in the process of substitution of side-chain fluorinated polymers in DWRs that generate emissions of hazardous PFASs. The research is intended to add to and complement the knowledge base generated in other sub-projects of SUPFES. Two research objectives were formulated: i) to provide improved decision support regarding the environmental performance[2] of the DWR alternatives, taking a holistic approach by the inclusion of a life cycle perspective, ii) to investigate public readiness for substitution and which messages can motivate consumers towards voluntary substitution.

The research was method-driven as, on a general level, the type of methods to apply were specified beforehand. LCA was used to include a life cycle perspective in the CAA, and a web-based questionnaire was used to study the effect of different types of messages on the willingness of consumers to enact substitution. Detailed method choices were goal-driven and are further described in theory and methods (chapter 2) as well as in each paper.

The research objectives were formulated as research questions. The first research objective, to generate a holistic decision support, corresponds to research questions 1-2, and the second research objective, the identification of messages that motivate consumers, corresponds to research question 3.

Research questions:

1. How can life cycle impact assessment (LCIA) of (eco)toxicity be strengthened to improve the relevance of LCA as a decision support in the chemical substitution of hazardous PFASs in textile applications?

2. How different is the environmental performance of the alternative DWRs compared with side-chain fluorinated polymer based C8 DWRs?

3. What type of information would motivate consumers towards the substitution of hazardous PFASs found in outdoor garments?

[2] In this context, and hereinafter in this text, environmental performance will include effects on ecosystems and human health.

1.4 Thesis structure

The research conducted to meet the aim of this thesis resulted in six papers (see list of publications, p.V), briefly described below. The papers are provided in full as appendices. The introductory chapters of this compilation thesis (*i.e.* the 'Kappa') synthesise the results presented in the papers. The substitution of hazardous PFASs in DWRs was the basis of the research in papers I, II, III, IV, and VI, and this substitution functions as an illustration and example throughout these introductory chapters. The issue at stake is introduced in Chapter 1 to provide relevant background to the synthesis and discussion, and the underlying theory and methods are presented in Chapter 2. The research questions are answered in Chapter 3. This is followed by a discussion of the implication of those responses to the overall aim and research objectives in Chapter 4 (4.1). The life cycle perspective in the research was implemented in a CAA with the use of LCA. The strengths and weaknesses of this approach are also covered in the discussion (4.2), as are implications for the use of LCA in this context (4.3). The discussion is concluded with an outlook based on case study experiences, including a proposition on how life cycle thinking can be applied in CAA (4.4). Chapter 5 contains concluding key messages, and future research needs are identified in Chapter 6.

A mapping of DWRs on the market is described in **Paper I**, including the main structure-property relationships of the DWRs, their diffuse emissions, and related hazards. This study was key in the CAA of the alternatives to DWRs based on side-chain fluorinated polymers that are precursors to long-chain PFAAs. This was the starting point for the research conducted in the SUPFES project. The findings steered further research to a potential problem shift between DWR alternatives, and the potential for consumer action was identified.

Life cycle impact assessment (LCIA) characterisation factors (CFs) for textile-relevant chemicals were calculated in **Paper II**. A generic data collection strategy is proposed in the paper, applicable also in fields other than textile.

A framework for LCIA of a subset PFASs is proposed in **Paper III**. The need for this framework was identified as the generic procedures applied in the calculation of CFs as described in Paper II required additional adaptations to capture PFAS-specific characteristics.

Both fluorinated and non-fluorinated DWRs in textile applications are evaluated in the case study of LCA application in CAA in **Paper IV**. This study predicts and

contrasts life cycle (eco)toxicity impacts, including use-phase diffuse emissions, with life cycle impacts in other categories such as climate change.

Paper V presents a review of how chemical risk assessment and LCA have been used in combination. This review includes the important characteristics of each method together with the potential pitfalls of their combination.

Paper VI explores the rhetoric required to motivate consumers towards voluntary substitution. Swedish willingness-to-pay for a garment without hazardous fluorinated chemicals is investigated using an experimental set-up.

2 Theory and methods

The key methods in relation to the research aims of this thesis, and their background, are elaborated here. The first sections of the chapter (2.1-2.5) cover theory and methods related to research objective i) to provide improved decision support regarding the environmental performance of the DWR alternatives, taking a holistic approach by the inclusion of a life cycle perspective. The second part (2.6-2.7) covers aspects related to research objective ii) to investigate public readiness for substitution and which messages can motivate consumers to voluntary substitution. The methods applied in each study are described in detail in each paper.

2.1 Precaution or exposure prevention

The assessment of the environmental and human health impacts of chemicals is generally based on a description of the cause-effect chain from emission to (eco)toxicological effect. Despite the uncontested idea of such a cause-effect chain, decision making regarding chemical risks takes different starting points. Tukker (2002) has described this in terms of framing, where actors in the 'precautionary frame' consider toxicity assessment as so fallible that effect assessments are hardly feasible, while actors in the 'risk assessment frame' view final effects as possible to meaningfully assess. Actors in civic society, *e.g.* non-governmental organisations (NGOs), and policy makers generally favour precaution, while actors in the industrial sector often favour the risk-based approach to risk reduction (Lissner and Romano, 2011).

The precautionary principle means taking preventive action despite uncertainty. Definitions of the precautionary principle vary depending on context (Bourguignon, 2016, Hansen *et al.*, 2007). One use of the principle in a chemical safety context is to stipulate action before a causal link has been established between chemical emissions and their effects on human health or the environment (as *e.g.* in the Ministerial Declaration of the Third International Conference on the Protection of the North Sea (EEA, 1990)). Acting on hazard information is precautionary in the substitution context, acknowledging uncertainties associated with risk containment measures. For example, collecting PFAS-contaminated wastewater at firefighting training sites could reduce environmental contamination, but risks will reoccur if that process is inefficient or subject to failure or accidents. The precautionary alternative, *i.e.* discontinuation of the use of PFASs, would eliminate the risk.

Both the precautionary frame and the risk assessment frame are relevant for the research presented in this thesis. A hazard assessment was made in Paper I, placing the starting point of this research in a precautionary context by highlighting hazards

associated with the water-repellent chemicals in the different DWR systems, but not assessing the relative risk that negative impact would manifest. The LCA and related research (Papers II-IV), on the other hand, are rooted in the risk assessment frame (more about this in 2.5.1), but these are given a precautionary character by the incorporation of emerging toxicity data in the LCIA (Papers III and IV). The use of LCA as a tool in CAAs can become a combination of the precautionary and risk assessment frames, as a substitution is made to remove a hazard, while the comparison of potential impacts, as is in an LCA, can be placed in the risk assessment frame (Tukker, 2002).

2.2 Chemical substitution

Chemical substitution is motivated by environmental and/or health risks (see definition by Hansson *et al.* (2011) in 1.1.2). Even within this rather narrow scope, the definition of substitution depends on the context, where some definitions include risk reduction by management practices while others include only the exchange of a substance of concern with a better alternative (Lissner and Romano, 2011). Substitution can be described as the reduction of risk or hazard, depending on the context (see 2.1).

In general, a substitution follows the process flow described for substitution under REACH (Figure 3). Depending on the context, the steps in the substitution process (1-5 in Figure 3) can be further detailed, and specific methods and/or models can be recommended for use (see e.g. Jacobs *et al.*, 2016). Learning from a history of regrettable substitutions (examples were given in 1.1.2), increasing focus is on alternatives assessment (Tickner *et al.*, 2019b). Alternatives assessments are, however, often hindered or slowed down by a lack of information. While relevant as part of a risk management strategy, the proportionality principle for information requirements (*e.g.* under REACH where reporting requirements are proportional to the rate at which each chemical is manufactured or imported) creates a regulatory lock-in where low-use (newly introduced) chemicals are not well tested. Method development is ongoing, as CAA is gaining international recognition as a research and policy field, addressing issues related to data shortage and other challenges (Tickner *et al.*, 2019a).

The concept of substitution rests on the assumption that a product is necessary, *i.e.* that its function must be delivered but with less environmental and human health impact. It has been proposed that the functionality criterion, *i.e.* that the alternative must provide at least the same function as the original product, may have to be re-assessed for a substitution to be sufficiently efficient from an environmental/human health perspective (Hansson *et al.*, 2011). It can also be argued

that certain functions, and subsequently certain chemicals and products, are simply not necessary and should be avoided and removed without substitution. The starting point in this thesis is that chemical substitution is done when a function is needed. Therefore, the results are discussed in relation to the concept of essential use as described by Cousins *et al.* (2019b).

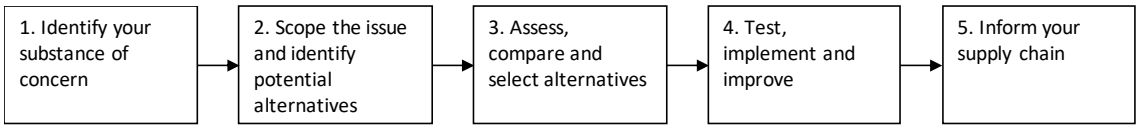

Figure 3: Generic substitution process as described under REACH (ECHA, 2020a)

2.3 Hazard assessment

Hazard assessment is key in CAA (Jacobs *et al.*, 2016). Hazard assessments can have different focuses, depending on their application area. In general, physical hazards, (eco)toxicity, environmental persistence, and bioaccumulation are assessed. Substances that qualify as persistent, bioaccumulative, and toxic (PBT), or very persistent and very bioaccumulative (vPvB), have long been recognised as hazardous to the environment and human health. The potential for irreversible contamination provides the basis for a new hazard identifier: persistent and mobile (PM, or very persistent and very mobile, vPvM) chemicals (UBA, 2017).

There are several hazard assessment methods available, both within regulatory contexts and for commercial purposes, *e.g.* Design for the Environment programme (DfE, US EPA (2011)), GreenScreen (Clean Production Action, 2013), and the GHS Column Model (IFA, 2014). A chemical's properties are assessed in relation to a number of hazard criteria in these assessment procedures. This is done within the broader categories physical hazards, (eco)toxicity, and environmental fate. The DfE were used in the hazard assessment conducted in the present research (Paper I). The DfE criteria are, to a large extent, based on globally accepted criteria in the Global Harmonisation System (GHS), and they are very similar to the GreenScreen method used by actors in the DWR industry.

The starting point of hazard assessment can be the full ingredient list of a chemical product, including residuals/impurities and degradation products. The hazard assessment in Paper I, however, focused on the DWR water-repellent component and other components of the DWR were evaluated in the LCA (Paper IV). This approach, which has a focus on the use phase, was selected because the use phase was the focus of this particular case study (Paper I). The use phase was a relevant starting point in a

generic evaluation of DWRs as it thoroughly assessed the water-repellent constituents of the chemical products. Once the water-repellent ingredient has been selected, auxiliary chemicals can be selected based on relevant environmental and human health criteria.

2.4 Life cycle perspectives in chemical alternatives assessment

A life cycle perspective implies cradle-to-grave considerations of a product. The application of a life cycle perspective in CAA guidance is divided into life cycle thinking and LCA (Jacobs *et al.*, 2016). In life cycle thinking, the cradle-to-grave implications of activities are considered, often qualitatively, without the details of an LCA (Baumann and Tillman, 2004). Life cycle thinking can be key in all steps of the substitution process (Figure 3). The National Research Council (2014) guidance, for example, gives brief guidance on the assessment of shifts in (eco)toxicity impacts between substances or life cycle stages due to differences in the 'synthetic history' of the chemical and on a broader product system mapping to identify differences between products with the chemical of concern and its alternatives. LCA however, is generally implemented as an 'add-on' assessment once safer alternatives have been identified, *i.e.* as an advanced part of the assessment of alternatives (Jacobs *et al.*, 2016). The application of an LCA is described by Jacobs *et al.* (2016) as a method to evaluate potential impacts in categories other than (eco)toxicity, *e.g.* climate change. (Eco)toxicity aspects related to changes in a product's life cycle, beyond the chemical of concern and its substitute, are, however, mentioned in *e.g.* the National Research Council (2014) guidance. Therein LCA (eco)toxicity indicator results are highlighted as different from hazard and risk assessments of alternatives (part of pre-LCA steps of the guidance) and are called 'directional indicators', *i.e.* indications of the relative magnitude of hazardousness of flows released to the environment.

2.5 Life cycle assessment

LCA provides a structured way to quantify potential impacts from resource extraction and emissions generated by activities (processes) within a product's life cycle. Environmental LCA covers environmental and human health impacts. This method can be complemented with 'S-LCA' to assess social impacts (Jørgensen, 2013) and life cycle costing, LCC, to provide an economic perspective (Kirk and Dell'Isola, 1995). An environmental LCA was conducted in the present research and is the method in focus below.

LCA is conducted as an iterative, four-step process, as illustrated in Figure 4. The LCA method is described in more detail in other texts (ex. Baumann and Tillman, 2004, Finnveden *et al.*, 2009) and is only briefly covered here. The first step is setting the goal and scope of the study, including defining the functional unit, system boundaries, relevant cut-off rules on what flows to include, and the impact categories to include in the study. The functional unit, the basis of comparison in an LCA, is a key element allowing for the comparison of essentially different systems that provide the same function. All environmentally relevant flows related to processes from the manufacture of materials and chemicals to the use and waste handling of the product, within relevant system boundaries, are quantified in a life cycle inventory (LCI). Those flows are characterised in an LCIA for their potential impacts on selected (potentially a broad range of) impact categories. Results can be normalised internally (*e.g.* to a benchmark) and/or externally (*e.g.* to the total amount of pollutants emitted in a region). LCIA results can also be aggregated in a weighting step. The broad scope of most LCAs, which are intended to cover all relevant impacts of all processes in a full life cycle, make it necessary to find appropriate simplifications. The assessment of environmental impacts in LCAs is, in general, not site-specific and flows occurring at different points in time are aggregated. Hence, an LCA can be used with the intention of capturing potential impacts per functional unit to allow comparative interpretations, *i.e.* the identification of hot spots or trade-offs within or between life cycles. The LCA, in its traditional execution, does not predict what will happen at a specific location.

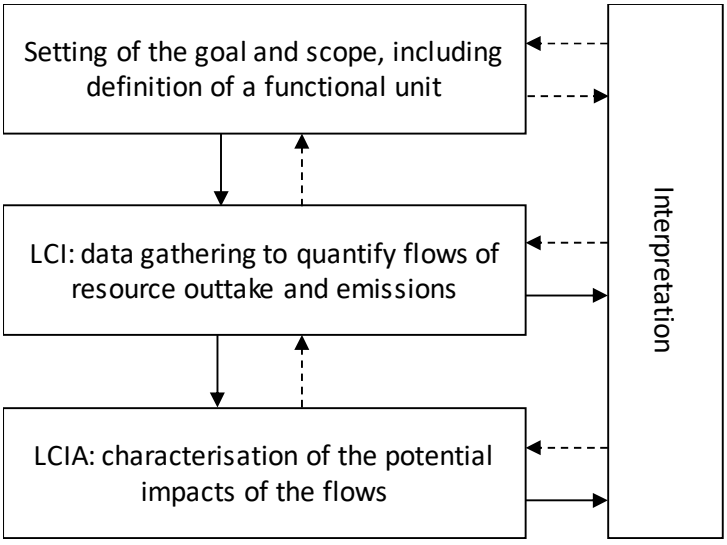

Figure 4: The iterative four-step process of LCA. The characterisation can be followed by a weighting step. LCA = life cycle assessment, LCI = life cycle inventory, LCIA = life cycle impact assessment

There are standards describing principles and structures for LCA. Examples are ISO 14040, 14044, and the EU Product Environmental Footprint (PEF) recommendations (2013/179/EU). Although an LCA conducted within a research context can follow the standard in all essential parts, it can be worthwhile to allow it to go beyond the structures of the standard in order to answer specific research questions. The LCA reported in Paper IV follows the general principles outlined in the ISO standards but was not set up for full standard compliance. For example, ISO 14044:2006 stipulates that a characterisation model should be '…based upon a distinct identifiable environmental mechanism and reproducible empirical observation' (4.4.2.2.3 e). In the LCIA framework proposed in Paper III, in contrast, empirically observed degradation patterns provided the basis for a model (see Table 1 in Paper III) that instead applied simplified degradation patterns. This was justified by the aim to fill data gaps.

An LCA of a product system intended to capture potential impacts of that system as it was during a certain time window is often referred to as an attributional LCA (or an accounting LCA). Curran *et al.* (2005) define attributional LCAs as being based on LCIs that '…attempt to answer "how are things (pollutants, resources, and exchanges among processes) flowing within the chosen temporal window?" '. Such LCAs are typically additive, *i.e.* LCAs of two materials can be added to get an LCA of the composite. An LCA that is instead intended to capture potential impacts of a change is often referred to as a consequential LCA (or change-oriented LCA). Curran *et al.* (2005) define consequential LCAs as being based on LCIs that '…attempt to answer "how will flows change in response to decisions?" '. Such LCAs contain only the processes affected by the change and are typically not additive. Consensus is yet to be reached on the applicability and data selection principles for these modelling choices (Ekvall *et al.*, 2016). Tillman (2000) and Ekvall *et al.* (2005) have suggested the terms retrospective and prospective LCA for accounting and change-oriented LCAs, respectively. Attributional LCAs have, however, been used in prospective studies (Arvidsson *et al.*, 2018). Thus, both attributional and consequential LCAs can be used to assess the recent past as well as future situations (Weidema, 2003). Marginal data are often suggested as the relevant choice for consequential modelling. This is, however, not always the case, and it is the goal of the study that must guide the choice; expected future average can be a better choice for long-term strategic planning (Tillman, 2000). Attributional LCAs can include allocation (*i.e.* the partition of environmental impacts between multiple process inputs or outputs), as the use of the method seeks to cut out the piece of the total global environmental exchanges related to the functional unit (Weidema, 2003, Fig. 1.3). Consequential LCAs, on the other hand, should include all activities affected by the change under study, and therefore,

these often rely on system expansion, *i.e.* the inclusion of additional functions to achieve a fair comparison (Ekvall and Weidema, 2004). The system under study can be divided into a foreground and a background system, where the foreground system can be defined as '…the collection of processes on which measures may be taken concerning their selection or mode of operation as a result of decisions based on the study' (Tillman, 2000). While the division into foreground and background systems can be described as something relevant only for prospective studies, as suggested by Tillman (2000), this is a concept more widely used and can also refer to a division of processes for which specific data are needed (foreground) and where generic data better capture an averaging effect across suppliers (background) (European Commission, 2010). The modelling choice between an attributional and a consequential LCA must be steered by the goal of the study and one should be aware that this makes it difficult to compare numerical results between LCAs unless they follow very consistent data collection and modelling procedures (*e.g.* environmental product declarations, EPDs).

In the LCA conducted as part of the research herein (Paper IV), the attributional, retrospective (recent past), approach was selected for two main reasons. By using attributional LCA, textile LCI data inventoried with a specific focus on chemical emissions by Roos *et al.* (2019) could be used in the model of the textile product chains. This method also allowed for comparisons within the life cycle of a garment, *e.g.* to elucidate the importance of DWR-related direct emissions to background emissions from energy generation. The LCA scope was broadened to increase the relevance of the (eco)toxicity impact assessment. Use-phase indirect emissions and transformation products were included in the study, in order to capture emission scenarios as depicted in Figure 1. This is normally not done in an LCA, not because the method itself does not allow for this but simply because data are not readily available, and sometimes also because awareness of the potential magnitude of those flows is low. Manufacturing processes of the foreground system were complemented with direct emissions of DWR-related chemicals, as identified in review in Paper I.

The uncertainty around LCA results can be large, and the size of this uncertainty can be difficult to quantify and communicate. Some uncertainties might even be impossible to quantify, such as impacts of catastrophic events or events in the far future. Dealing with uncertainty in LCA is about 'getting the right numbers', *i.e.* working with accurate data, and 'getting the numbers right', *i.e.* the precision of the data (Figure 5). Getting the numbers right in an LCA is about representativeness, reliability, considerations of temporal and spatial variability, data gaps, model

uncertainty, and minimising errors. Getting the right numbers is about making the LCA result capture meaningful characteristics of a system. The overlap between the two types of contributors to uncertainty stem from the complexity of an LCA, *i.e.* that data are used in different parts of an aggregated model, and depending on where data gaps, issues with representativeness, or model uncertainty exist, this could affect the accuracy or precision of the final result. Quantitative uncertainty assessment is technically feasible (Mendoza Beltran *et al.*, 2018, Groen *et al.*, 2017, Ciroth *et al.*, 2004, Igos *et al.*, 2018), *e.g.* using statistical approaches, such as global sensitivity analysis (Groen *et al.*, 2017). However, the data basis seems to seldom allow for this assessment method (Heimersson *et al.*, 2019, related work to this thesis, see p.V item D).

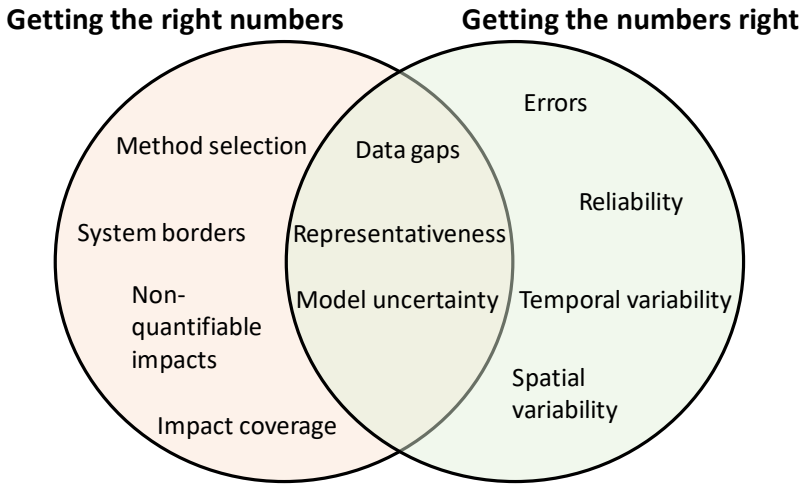

Figure 5: Factors contributing to uncertainties in LCA classified into two overlapping fields representing accuracy, or 'getting the right numbers' and precision, or 'getting the numbers right'. This is a Figure from Heimersson et al. (2019, related work to this thesis, see p.V item D).

2.5.1 Chemical risk in a life cycle assessment context

It is a common understanding that an LCA does not deal with risk (see *e.g.* Baumann and Tillman, 2004). An LCA, in its traditional execution, does not assess the acceptability of risk. Neither is it in its traditional execution used to assess real consequences, in terms of trying to reflect the time and place where impacts will occur, something that is associated with the term risk (Klinke and Renn, 2002). The disconnection in time and place has its purpose, as the goal of any LCA is founded on a comparison (within or between life cycles), and thus it is more important that the comparison is robust than that the outcome reflects temporal and spatial detail. Thus, while an LCA can be a relevant tool in the risk management toolbox, it does not, in its traditional execution, predict what will happen at a specific location. While the same

cause-effect chains are modelled in an LCA and a risk assessment, the modelling approach depends on the environmental assessment method.

Chemical fate and exposure considerations in an LCA often lack geographical resolution for practical reasons; it is seldom reasonable to collect data on a very detailed level either because such data do not exist (yet), and/or because the study would have enormous proportions given the often global nature of supply chains and product use. This is not unique to an LCA, and the same applies to large-scale chemical risk assessments (CRAs), *e.g.* CRAs conducted under REACH, in which generic exposure models are applied. In fact, the very same fate and exposure models can be used in CRAs and LCAs (see *e.g.* the exposure and fate module of the USEtox model (Rosenbaum *et al.*, 2008) that build on SimpleBox, which is a model that is also used as part of the chemical evaluation under REACH).

Effect considerations can be expressed in different ways in an LCA, depending on the LCIA method used. Effects considered are intended to be relevant for human health/environment, but data selected are not necessarily conservative (*i.e.* cautious), and the robustness of the estimate is important. For example, averages across species can be used to construct an ecotoxicity CF instead of the datum for the most sensitive species, to construct an effect metric (Henderson *et al.*, 2011). Safety factors are generally not used. However, while such average values can be more robust in the sense that additional data will have little effect on the CF, this approach can lead to a CF of low accuracy for chemicals with a specific mode of action (*i.e.* non-narcotics). For example, a herbicide may be highly toxic for algae but not for fish and invertebrates, and thus an average effect metric across species will not reflect the possible ecosystem damage from the toxic effect on primary producers (photosynthesising organisms). Effect thresholds are generally disregarded as the dose-response curve is linearized, allowing for the quantification of marginal incremental impacts. In theory, a non-linear approach would also be possible in an LCIA, but this would require knowledge of background exposure (*i.e.* exposure to pollution from life cycles other than the one(s) under study).

2.5.2 Life cycle impact assessment of (eco)toxicity

The inclusion of (eco)toxicity effects in an LCIA is a process that has been ongoing for a couple of decades. A number of LCIA methods that cover (eco)toxicity are now available (European Commission, 2011), *e.g.* the ecological scarcity method (Frischknecht and Knöpfel, 2013), EPS (Steen, 2019), Ecoindicator99 (Pre-sustainability, 2000), Impact 2002 (Jolliet *et al.*, 2003), EDIP 2003 (Potting and Hauschild, 2005), MEEUP (Kemna *et al.*, 2005), ReCiPe (Huijbregts *et al.*, 2017), CML

(Huijbregts *et al.*, 2000), TRACI (Bare, 2011), and USEtox (Rosenbaum *et al.*, 2008, Hauschild *et al.*, 2008).

The USEtox model and associated databases with CFs were used in the research presented in Papers II, III, and IV and is the LCIA (eco)toxicity model in focus below. The USEtox model has been recommended for use within the EU (European Commission, 2011, Saouter *et al.*, 2018) and is provided in a format allowing for the calculation of additional CFs. The USETox model is a multimedia-nested box model for transport and fate calculations and the estimation of LCIA CFs that combine those calculations with dose-effect information. The model is a result of a UNEP Life Cycle Initiative effort and is a consensus model incorporating harmonised components from several (eco)toxicity assessment models (Hauschild *et al.*, 2008, Westh *et al.*, 2015). Hence, USEtox contains model components from other (eco)toxicity LCIA models (CalTOX, IMPACT 2002, USES-LCA, and EDIP97; Hauschild *et al.* (2008)), and more recent versions of some of the other models make use of USEtox CFs.

USEtox model versions 1 and 2 (2.12 was the latest version at the time of writing) include human health cancer and non-cancer, and ecotoxicity freshwater indicators. As part of the UNEP Life Cycle Initiative, Fantke *et al.* (2018a, work related to this thesis, see p. V item C) have identified the need to add elements to the USEtox model, including marine effects (one reason being to capture potential impacts of persistent and mobile chemicals such as PFASs), effects on sediment-dwelling organisms, soil organisms, and pollinating insects and other species of special concern. Also as part of the UNEP Life Cycle Initiative, Fantke *et al.* (2018b) have identified the need to include direct human exposure pathways and to account for background exposures in the dose-response assessment. With the reviews (Fantke *et al.*, 2018a, Fantke *et al.*, 2018b) as background, Owsianiak *et al.* (2019) and Fantke *et al.* (2019) have formulated recommendations on further model developments that will lead to updates of the USEtox model.

CFs are calculated in the USEtox CF calculation framework by multiplying matrices containing fate factors (FFs), exposure factors (XFs) and effect factors (EFs), Equation 1. Intake fractions (iFs), a summary metric of human exposure in relation to emissions, are calculated by matrix multiplication of FF and XF matrices.

Equation 1: $CF = FF \times XF \times EF$

FFs describe chemical partitioning, dispersion, degradation, and transport in and between the various environmental compartments and are expressed in days [d] interpreted as the chemical residence time in a given compartment. For ecotoxicity, XFs are expressed as the mass fraction dissolved in water [$kg_{dissolved}/kg_{in\ compartment}$]. The dissolved fraction is all of the substance present in the compartment that is not associated with suspended particles, dissolved organic carbon (DOC), or bioaccumulated in biota (bioaccumulation relevant for ecotoxicity is considered in the EF, that represents long-term exposure conditions). EFs describe the potential affected fraction (PAF) of aquatic species integrated over exposed water volume and time [PAF $m^3/kg_{dissolved}$]. The iFs for human toxicity are expressed as intake via inhalation or ingestion per unit mass emitted [$kg_{intake}/kg_{emitted}$]), and EFs are expressed as cases per unit mass intake [$cases/kg_{intake}$]. Additional documentation on the USEtox model can be found elsewhere (Rosenbaum *et al.*, 2011, Henderson *et al.*, 2011, Rosenbaum *et al.*, 2008, Fantke *et al.*, 2017).

A 'time-integrated' steady-state exposure is modelled in the USEtox model to have effect on organisms in the environment. Degradable substances disappear while persistent substances accumulate. While the model calculates losses via degradation, it is up to the modeller to identify and include relevant degradation products. van Zelm *et al.* (2010) have shown in a case study that the exclusion of degradation products could lead to an underestimation of potential impacts by orders of magnitude. Roos *et al.* (2019) have approached this by constructing time-integrated recipes for textile products that include both primary pollutants and degradation products. While the inclusion of degradation products can be highly relevant, detailed guidance on how to make such inclusions is missing, and LCA databases rarely (if at all) contain an account of the emissions of transformation products.

Part of the USEtox project is the publication of databases with USEtox CFs. Current versions of the databases (2.12) contain 3077 organic and 27 inorganic substances (www.usetox.org). Other database providers use the USEtox model to calculate CFs for additional substances, *e.g.* the COSMEDE database that covers 7815 cosmetic and detergent substances (ADEME and CYCLOeco, 2020). These are large databases, nevertheless, they cover only a small share of the chemicals on the market - over 350 000 chemicals and mixtures have been registered for production and use (Wang *et al.*, 2020).

2.5.3 Life cycle assessment of textile products

Textile product chains are almost without exception global (Börjeson, 2017). See Figure 6 for a simplified product chain (*i.e.* life cycle of a garment). Textile production is infamous for its social and environmental impacts (Muthu, 2014) and the opacity of its global supply chain (Börjeson, 2017). Textile manufacturing stages are associated with discharges of large volumes of polluted water carrying toxic chemicals (European Commission, 2003). (Eco)toxic impacts of textile products have seldom been included in textile LCAs, due to significant gaps in the available data on chemical emissions related to textile manufacture, use, and end-of-life, and their (eco)toxicity potential (Roos *et al.*, 2015a). Recent research has, however, improved the situation (see e.g. Roos, 2016, Sandin *et al.*, 2019, Roos *et al.*, 2015b).

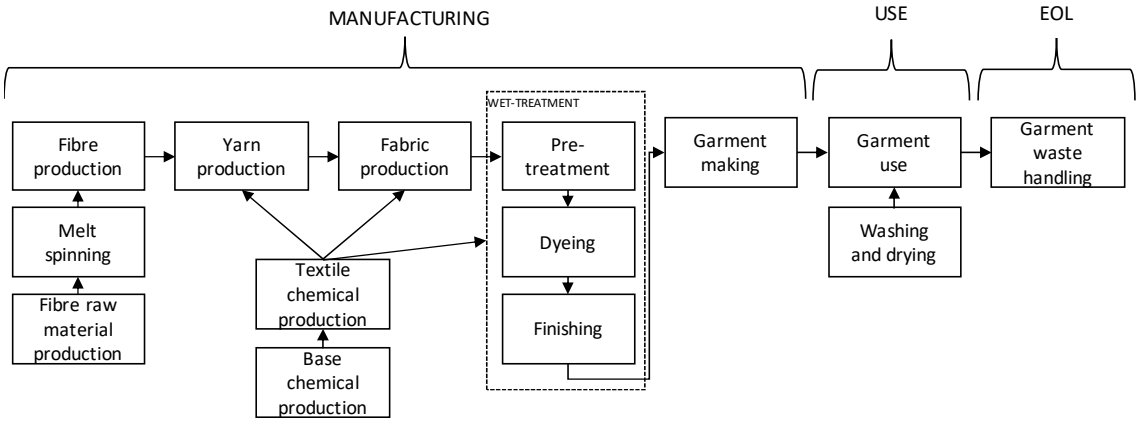

Figure 6: Simplified product chain (life cycle) of a garment. EOL = end of life

The proposal of a data collection strategy and calculation of textile chemical CFs (Paper II), and application of the Roos *et al.* (2019) inventory framework in a case study (the LCA of Paper IV) are contributions to the above-mentioned developments.

2.6 Value-belief-norm theory in risk communication

Communicating chemical risks is not an easy task. The reason for communicating risks can be to create acceptance, *e.g.* public acceptance of the risks associated with nuclear power (*e.g.* Tanaka, 2004, Löfstedt, 2005), or it can be done to create action, *e.g.* change people's car driving habits to reduce greenhouse gas emissions (*e.g.* Krantz Lindgren, 2001), or as in the case relevant herein, to motivate consumers for voluntary substitution of hazardous PFASs. Either way, to create the response intended, the message must come through. This is not as easy as simply presenting the right numbers (Fischhoff, 1995, Adler and Pittle, 1984), such as results from a hazard assessment or an LCA. The prior knowledge levels (Snyder, 2001),

values, beliefs, and norms of the recipient of the information play a crucial role (Stern, 2000), as does trust in the communicator (Löfstedt, 2005).

It is an often-expressed opinion that information campaigns are not effective (Rice and Atkin, 2012). Even so, information campaigns are a re-occurring risk-management strategy. As part of the SUPFES project, public communication to achieve source control in municipal wastewater treatment was in focus because diffuse sources of PFAS were hypothesised to be important. The project aimed to evaluate the potential to educate the public and formulate key messages comprehensible to the Swedish public. In order to achieve relevant results, *i.e.* to find out what will create attitude changes and pro-environmental behaviour (Jagers *et al.*, 2009), environmental attitudes of the Swedish public, in general as well as in relation to the specific case of PFASs in outdoor garments, were surveyed and results were evaluated in relation to existing theory on pro-environmental behaviour (PaperVI).

Research within the fields of sociology and psychology has tried to explain pro-environmental behaviour, or conservation behaviour, with various models. According to Kaiser *et al.* (2005) attitude-related theories have converged into two frameworks: the value-belief-norm (VBN) theory (Stern, 2000) and the theory of planned behaviour (Ajzen, 1991). Both of these theories have reported explained variances of approximately 20-30%. The VBN theory will be further expanded upon here as it was selected as the explanatory model in Paper VI.

The VBN-theory aims to '…inform efforts to promote proenvironmental behaviour' (Stern, 2000). The theory aims to explain non-activist environmentalism and links value theory, norm-activation theory, and the New Environmental Paradigm (NEP; Dunlap and Van Liere (1978)). In the VBN theory, values (biospheric, altruistic, egoistic) affect beliefs about adverse consequences for valued objects and the perceived ability to reduce threat (ecological worldview (NEP)) that in turn activate personal norms about pro-environmental behaviour that, lastly, affect behaviour (Stern, 2000 Fig. 1). Each variable can also affect variables further down the cause-effect chain. A central part of the VBN theory is that the norms of and predisposition to pro-environmental behaviour can be influenced by information if that can change the beliefs. People's environmental norms can be activated by highlighting certain values or consequences. As such, the VBN theory lends itself well to evaluate a suitable rhetoric, or different information framing, in information campaigns.

2.7 Information framing

Framing (or framing effects) is generally understood as a cognitive bias in which people react to a particular choice in different ways, depending on how it is presented (Tversky and Kahneman, 1981). For example, a choice can be presented as a loss or gain or simply as positively or negatively loaded information. Cognitive bias refers to a systematic pattern of deviation from norm or rationality in judgment, whereby inferences about other people and situations may be drawn in an illogical fashion. Individuals create their own 'subjective social reality' from their perception of input. How something is presented to the public influences the choices people make about how to act upon that information. Depending on how the outcomes at stake are valued, the description of the risk should be adapted (Pidgeon and Fischhoff, 2011). Selected information must be designed with the receiver in mind. The deficit model, that more information will generate the sought response, is intuitive but can erode trust if non-action is simply met with more information (Pidgeon and Fischhoff, 2011). The frame applied in an information campaign has the potential to affect how the information is received. Framing effects in a substitution context are further explored in Paper VI in a study of the willingness-to-pay for alternative garments.

3 Summary of thesis contributions in relation to research questions

3.1 How can life cycle impact assessment (LCIA) of (eco)toxicity be strengthened to improve the relevance of LCA as a decision support in the chemical substitution of hazardous PFASs in textile applications?

The inclusion of (eco)toxicity impacts in LCA requires data on chemical emissions related to the functional unit and CFs to characterise the impacts of those emissions. Roos *et al.* (2019) have inventoried textile-relevant processes for chemical emission flows. No CFs were available in the USEtox or COSMEDE databases for 35% of those chemical flows (n=72) (see 2.5.2). CFs were calculated to allow for their inclusion in the LCIA in Paper II. Any new CF must be comparable to existing CFs, and thus the USEtox manuals (Huijbregts *et al.*, 2015a, Huijbregts *et al.*, 2015b) were the starting point for data collection. A data selection procedure was developed that introduced additional data sources as well as the possibility to include estimated data (in addition to empirical data) also for (eco)toxicity characteristics (Figure 7). The concept of Minimum Data Quality (MDQ) was introduced in acknowledgement of the additional uncertainty of CFs based on estimated or scarce data (cf. Holmquist *et al.*, 2018, related work to this thesis, see p.V item B). The CFs calculated in Paper II are for textile chemicals, but the data selection procedure can be applied to any chemical and, in that way, aid in filling important data gaps in the (eco)toxicity impact models used in LCIAs, including sectors other than textile. This increases the relevance of any LCA where emissions of hazardous chemicals has been assessed as relevant for evaluation.

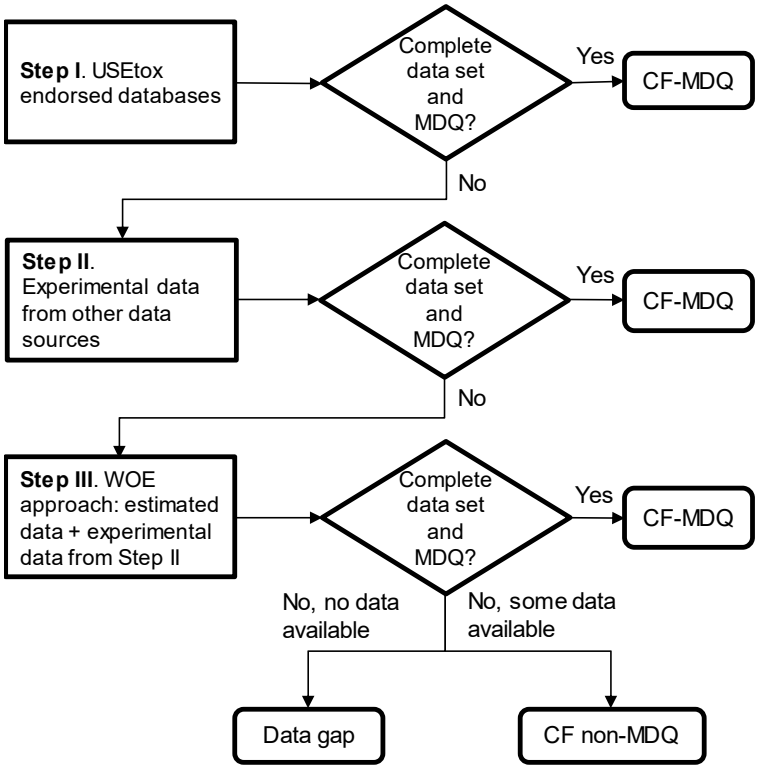

Figure 7: The three-step data source selection strategy developed in Paper II. WOE = weight of evidence, MDQ = minimum data quality, CF = characterisation factor. This is Figure 1 in Paper II.

The inventory by Roos *et al.* (2019) contains PFASs (PFAAs, FTOHs, and FTAs). It was acknowledged in Paper II that the special properties of these chemicals, their extreme persistence, and the amphiphilicity of the PFAAs, might need special considerations to achieve relevant CFs. No exceptions from the data collection procedure or adjustments of model algorithms were made within the scope of the study in Paper II. To allow for the inclusion those PFASs in the LCIA, an (eco)toxicity LCIA framework was developed (Paper III; Figure 8) that accounted for the special properties of PFASs (covering non-polymeric perfluoroalkane sulfonyl fluorides (PASF)-based and fluorotelomer-based substances and side-chain fluorinated polymers[3]).

[3] Paper III says that the LCIA framework can be applied to the 'vast majority of PFAS-containing products on the market'. In Paper III we were not considering fluoropolymers or perfluoropolyethers which comprise a significant fraction of the PFAS market. Consideration of the LCIA of fluoropolymers and perfluoropolyethers would be a valuable extension of our framework.

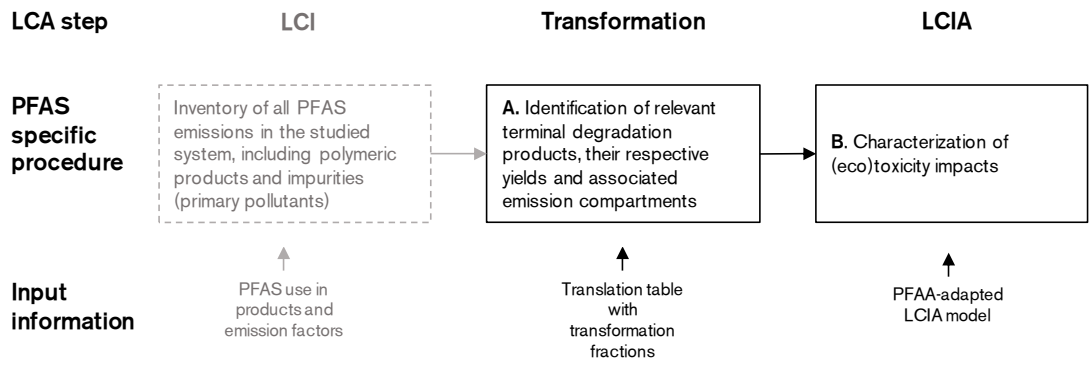

Figure 8: Illustration of the workflow of the framework proposed in Paper III. Detailed guidance was given for the black parts of the figure, grey parts were described in overview and exemplified in the case study. This is Figure 1 in Paper III.

The (eco)toxicity LCIA framework for PFASs had two main components;

A. A translation table to arrive at a long-term relevant inventory (*i.e.* time-integrated) of terminal degradation products (*i.e.* the PFAAs) and

B. An LCIA model adapted for PFAAs and CFs calculated for three important PFAAs: PFOA, PFHxA, and PFBS.

By applying the translation table, PFAA-precursors could be transformed into an aggregated LCI of PFAAs, that in turn could be characterised using the CFs calculated with a PFAA-adapted LCIA model.

The translation table (Table 1 in Paper III) was developed based on available literature reviews of degradation studies mapping the transformation of non-polymeric PFASs. While degradation pathways are diverse and differ between precursors and environmental media, they were highly simplified as part of the framework proposed in Paper III. All fluorotelomer-based substances with seven or eight perfluorinated carbon atoms in the alkyl chain were assigned PFOA, those with five or six perfluorinated carbon atoms were assigned PFHxA, and sulfonyl substances with four perfluorinated carbon atoms in the alkyl chain were assigned PFBS as the degradation product. The yield of PFAA from non-polymeric PFAS precursors was set to 60%. With this simplification, the more well-characterised PFAAs act as proxies for less well-studied substances. As side-chain fluorinated polymer degradation is a debated issue yet to be fully described by environmental chemists, the polymer degradation was set to 0-100%. Thus, if the starting point is a direct emission of 1 kg of 8:2 FTOH (a non-polymeric PFAS) to air, the translation table aids in converting this emission into 0.5 kg of PFOA to air (adjusted for the weight fraction of PFOA to 8:2 FTOH), which is the flow to be characterised in the PFAA-adapted LCIA model.

As part of the (eco)toxicity LCIA PFAS framework proposed in Paper III, the USEtox model was adapted to better capture PFAA fate, exposure, and effects. Adjustments were made to allow for the use of empirical data for the calculation of XFs and FFs instead of using the octanol-water partitioning coefficient (K_{OW}), which is not a relevant parameter to predict PFAA fate. Effects in the marine compartments were added to allow for the calculation of marine ecotoxicity indicator scores, as this is the main accumulation compartment of PFAAs in the environment. With this PFAA-adapted model, CFs were calculated for PFOA, PFHxA, and PFBS. The data collection for CF calculation was based on the data collection procedure developed in Paper II but taken further by the inclusion of data from a multitude of sources. As part of an uncertainty assessment, in addition to traditional laboratory derived rodent data, human epidemiological data were applied to calculate EFs using rough extrapolations. PFOA effect levels for cholesterol increase were used to calculate EFs. To arrive at EFs for PFHxA and PFBS, the EFs for PFOA were extrapolated based on human elimination half-lives.

A comparison of the PFAA CFs and CFs for all substances in the USEtox databases (Figure 9) shows that the PFAA CFs as calculated in Paper III are ranked among the top 5% for marine ecotoxicity. CFs for non-cancer human toxicity ranked equally high when based on epidemiological data but not when based on rodent data. The high ranking in the non-cancer human toxicity impact category, for CFs based on rough extrapolations from epidemiological data, reflects the high potential for human toxicity of the PFAAs, *i.e.* the high EF. The high ranking in the marine ecotoxicity impact category, in contrast, reflects ocean accumulation rather than high ecotoxicity, *i.e.* the high FFs for the marine compartment (*cf.* freshwater and marine ecotoxicity, Figure 9, lower panel).

Similarities and differences were identified in a comparison of the PFAA CFs calculated in Paper III with those calculated in Paper II (Figure 9). CFs calculated Paper II were fairly similar to those calculated in Paper III when non-cancer toxicity CFs were based on rodent-data EFs. CFs for non-cancer toxicity, based on rough extrapolations from epidemiological data, as calculated in Paper III, were, however, orders of magnitude higher than those calculated in Paper II. Marine ecotoxicity was not included in the USEtox model (2.02), hence, CFs for marine ecotoxicity were not included in Paper II. The high impact potential for human toxicity was not captured in Paper II as the data collection was designed to stop data collection when 'good enough' experimental data had been collected (Table 1 in Paper II), *i.e.* MDQ did not imply a complete data set but that experimental data had been found in a source assessed as relevant. Considerably higher potential for human toxicity was assigned to the PFAAs

in the uncertainty assessment in Paper III than in Paper II because the data collection strategy was much expanded, and due to further maturation of data (see further discussion in 4.2). The spread of CFs from Papers II and III shows that knowledge about a specific substance (or substance group) and extensive data collection efforts can drastically change the outcome of an LCIA. This spread in data is also an indication of how large uncertainties can be.

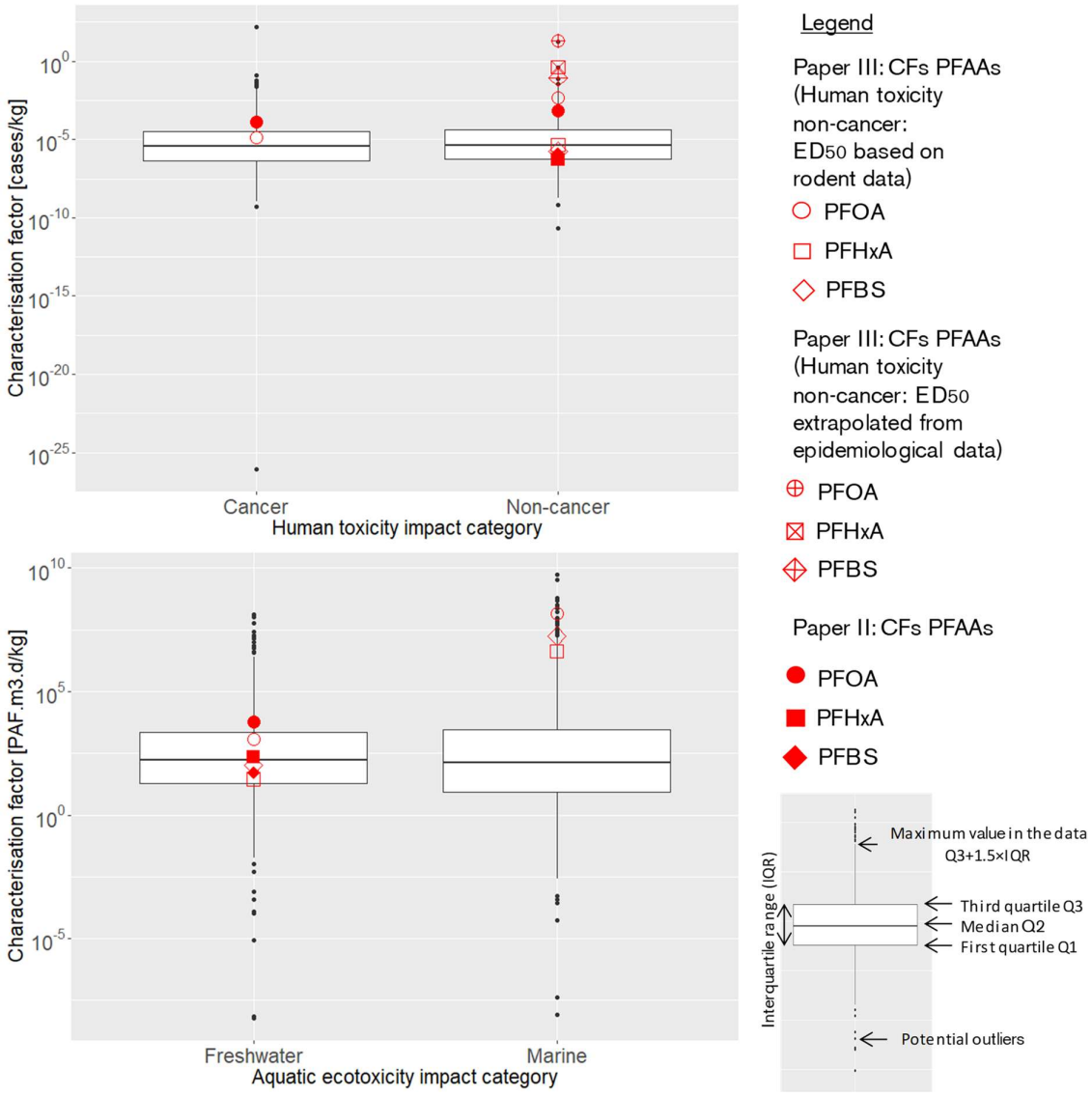

Figure 9: CFs for freshwater emissions for the three PFAAs (highlighted values) and their ranking in relation to boxplots of all CFs as calculated with existing USEtox® 2.1 databases for organics and metal ions, with a marine extension from Paper III. Human toxicity cancer (n=612) and non-cancer (n=441) in the upper panel and aquatic ecotoxicity (n=2523) in the lower panel. The cancer effects of non-carcinogenic chemicals are not displayed (i.e. zero values removed). Adapted from Figure 2 in Paper III.

The very high CFs in the human health non-cancer toxicity category (based on roughly extrapolated epidemiological data) had clear effects on the results of the LCA on DWRs (Paper IV), despite the low levels of use of PFASs in the studied application. The high CFs for marine aquatic ecotoxicity, in contrast, were also in the same range as the top 5% of the USEtox 2.1 database. However, the high CFs did not come through in the LCA results for two reasons. Firstly, the gap between the PFAA CFs and the CFs of the other substances in the database, most importantly metals that also accumulate in the oceans, was not as large. Secondly, according to the LCI, metals were emitted from most parts of the value chain, mainly due to energy generation, and therefore contributed to a large proportion of the predicted potential impacts. CFs calculated in Paper III showed that the PFAAs were ranked high in relative (eco)toxicity potential, but the results of the LCA in Paper IV showed that whether or not that high rank breaks through in the final LCA results depends on the LCI.

An issue relevant to the construction of PFAS-LCIs and other chemical emissions was highlighted in Paper III, namely the difficulty to obtain chemical emissions data. How to obtain emissions data was not part of the framework for Paper III, and this challenge is only described in the overview of the paper through suggested information sources on the use and emissions of PFASs. In a case study involving a simplified LCA on surgical drapes included in the paper for illustrative purposes, emission factors were applied to quantify PFAS emissions. LCI unit process data, other than energy-related processes, are not always inventoried for direct chemical emissions in LCA databases. Background data modelled using aggregated processes generally contain the chemical emissions of many different chemicals, but the absolute majority, if not all, often come from energy-related processes. It can be difficult for the LCA modeller to judge whether or not all relevant emissions have been included in the database process. Knowledge about the system is essential to identify where emissions are likely to occur. Process data from LCA databases can be complemented with direct chemical emissions with the application of generic emission factors, as was done in Papers III and IV. Arriving at a complete LCI is a necessary step before conducting an LCIA as the impact assessment otherwise would be limited by data gaps.

In summary, this thesis contributed an answer to research question one with practical and methodological developments:

i) Despite databases with 3000+ CFs (www.usetox.org), most chemicals on the global market remain uncharacterised in the LCIA context (see 2.5.2). CFs were calculated in Papers II and III and made available to LCA practitioners to fill data gaps with regards to CFs relevant in PFAS and textile applications.

ii) The several thousand missing CFs referred to above imply a continuous need to collect data on physicochemical and (eco)toxicological characteristics in a resource-efficient way that still generates relevant results. To address this need, a data collection strategy was proposed in Paper II that went to unprecedented lengths to fill data gaps, in particular for (eco)toxicity. This strategy demonstrated a consistent way for analysts to approach other chemicals.

iii) (Eco)toxicity impact models are generally based on 'standard' organic substance properties, *i.e.* fat-soluble non-surfactant characteristics. Certain substances (or substance groups) behave in radically different ways and require further data collection and model adaptions based on their special characteristics. One such group is the PFASs. To address the need of special PFAS considerations in LCIA, a framework was proposed in Paper III to derive a long-term relevant inventory of PFAAs and to calculate PFAA CFs.

How to know when additional data collection or model adaptions are needed is discussed in 4.3.

3.2 How different is the environmental performance of the alternative DWRs compared with side-chain fluorinated polymer based C8 DWRs?

The identification of relevant substances for further evaluation was the focus of Paper I. DWRs on the market were categorised into four main types (Figure 10); a) side-chain fluorinated polymer based DWRs b) silicone-based DWRs, c) hydrocarbon-based DWRs, and d) DWRs based on 'other chemistries' (not in Figure 10). Non-polymer substances related to the structural moiety of the substance that provide the water (and oil) repellency function to the DWR formulation, that could be predicted to be emitted in the use phase, were identified and assessed for their associated hazards

(Table 1). PFOA was identified as a relevant impurity and degradation product in DWRs based on a C8 side-chain fluorinated polymer, PFHxA from C6 and PFBS from C4. Short-chain silanols, dimethylsilanediol (DMSD) and trimethylsilanol (TMS), were identified as degradation products, and octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) were identified as possible impurities of the silicone-based DWRs. Paraffin wax was identified as a possible degradation product of the hydrocarbon-based DWRs. For DWR systems evaluated under the category 'other chemistries', degradation products and impurities could not be identified.

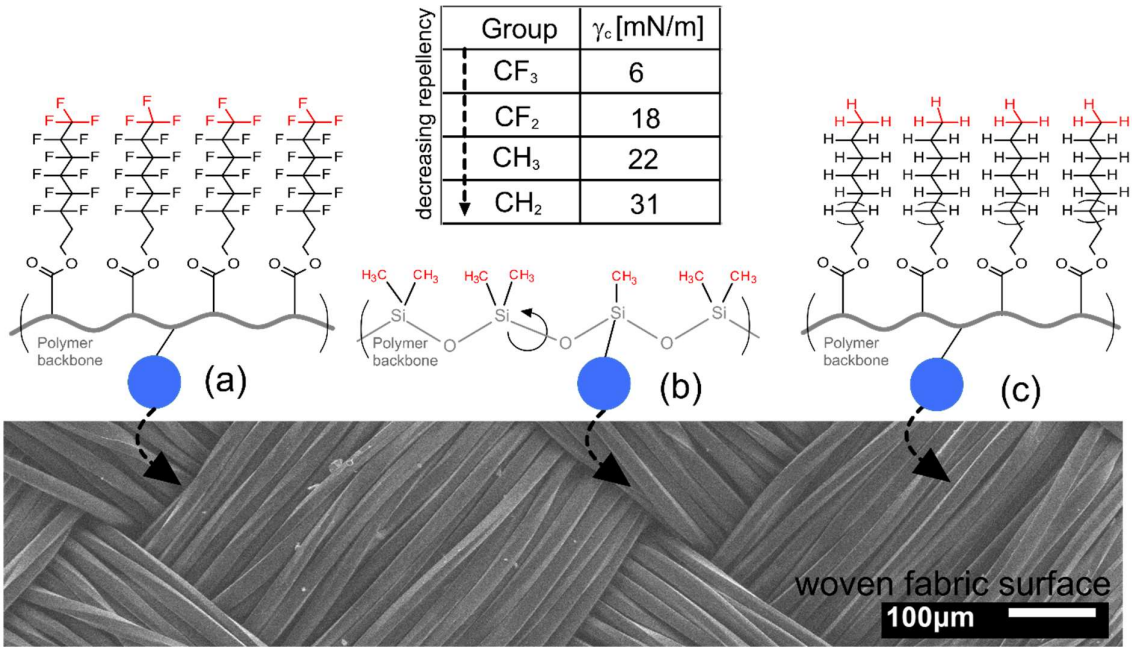

Figure 10: Raster electron microscopy (REM) picture (courtesy of Swerea IVF) of the structured surface of a synthetic fabric, and schematic pictures of the DWR polymers that deliver the final textile repellency (a–c): side-chain fluorinated polymer (a), silicone (b), and hydrocarbon (c). The polymers react, with the help of fibre-bonding groups (blue), with the surface of textile fabrics. Terminal groups with low critical surface energy (γc) (Fox and Zisman, 1950), CF_3 and CH_3 groups, need to be closely packed and orientated toward the surface. This is Figure 1 in Paper I.

The hazard assessment (Table 1) based on an extensive literature review showed that all alternatives to the benchmark PFOA were also associated with hazards. The short-chain PFAAs are less toxic but are as equally persistent as PFOA. The silicone-related substances are also persistent, and the cyclic siloxanes are toxic and bioaccumulative. The paraffin wax was the most environmentally benign, while the 'other chemistries' were not possible to assess due to lack of data and information on their detailed composition. Emissions of impurities and degradation products were predicted to differ between DWRs, both with regards to amount and further fate,

leading to differences in exposure, which was instead assessed within the scope of the LCA in Paper IV.

Table 1: Collated hazard assessment for selected DWR-related substances that reach the environment via diffuse emissions. Degradation products are denoted ♯, and impurities are denoted ¤. Hazard classification abbreviations are: vL=very low, L=low, M=moderate, H=high, vH = very high, PEA= potentially endocrine active, DG= data gap. Classifications in italics are of low confidence, and those in bold are of high confidence. Classifications based on estimated data are marked with an asterisk (*). Endpoint abbreviations are C = carcinogenicity, M = mutagenicity/genotoxicity, R= reproductive toxicity, D= developmental toxicity, E=endocrine activity, AT=acute mammalian toxicity, ST=repeated dose toxicity, N=neurotoxicity, AA=acute aquatic toxicity, CA=chronic aquatic toxicity, P=environmental persistence, and B=bioaccumulation. Adapted from Table 3 in Paper I.

Substance	Hazard classification per endpoint											
	Human health								Ecotox		Fate	
	C	M	R	D	E	AT	ST	N	AA	CA	P	B
Benchmark												
PFOA #¤	H	L	*H*	H	PEA	M	H	DG	L	*L*	vH	H
Side-chain fluorinated polymers												
PFHxA #¤	*L*	L	*M*	*M*	PEA	L	*M*	DG	*L*	*L*	vH	L
PFBS #¤	DG	L	*L*	L	PEA	L	*L*	DG	*L*	*L*	vH	L
Silicones												
Short-chain silanols ♯	DG	DG	DG	DG	DG	DG	DG	DG	DG	DG	DG	DG
DMSD #	DG	DG	DG	DG	DG	DG	*M*	DG	DG	DG	*vH*	*L**
TMS #	DG	*L*	DG	*L*	DG	M	*M*	DG	L	DG	DG	*L**
D4 ¤	L	*L*	*L*	L	PEA	L	H	DG	*L*	vH	vH	*vH*
D5 ¤	L	L	L	L	PEA	*H*	H	DG	L	*L*	vH	*vH*
Hydrocarbons												
Paraffin Wax #	L	L	*vL**	*vL**	DG	L	*M*	DG	*L**	*L**	L	*L**
Other chemistries												
Unknown	DG	DG	DG	DG	DG	DG	DG	DG	DG	DG	DG	DG

In the LCA (Paper IV), five DWR systems were selected for assessment; two types of side-chain fluorinated polymers (C4 and C6), one silicone based, one hydrocarbon-based wax and a non-fluorinated based on hyperbranched polymers. The results of the LCA in Paper IV showed that DWRs can be differentiated on a whole garment basis for the human health non-cancer toxicity category indicator if the CFs based on roughly extrapolated epidemiological data were used (but not if the analysis were restricted to rodent data EF based CFs), but not for the other categories (Figure 11, upper panel, only climate change and (eco)toxicity shown). The indicator scores in the human health non-cancer category for the fluorinated DWR systems (C8, C6, and C4) were one to three orders of magnitudes higher (using the roughly extrapolated CFs) than for the non-fluorinated systems. The DWR was used in very small amounts

compared to the other materials in the garment, thus a chemical must have very high potency to affect end results, as may be the case for PFOA (emitted from the benchmark system C8) in particular but also for PFHxA and PFBS, emitted from the C6 and C4 systems, respectively. Looking instead at the results of only the finishing processes, DWR systems were again indicated to be possible to differentiate in the non-cancer impact category (Figure 11, lower panel, only climate change and (eco)toxicity shown). Differences between DWR systems in the other categories were larger compared to when the whole garment was included but may reflect uncertainty rather than actual differences between DWR systems.

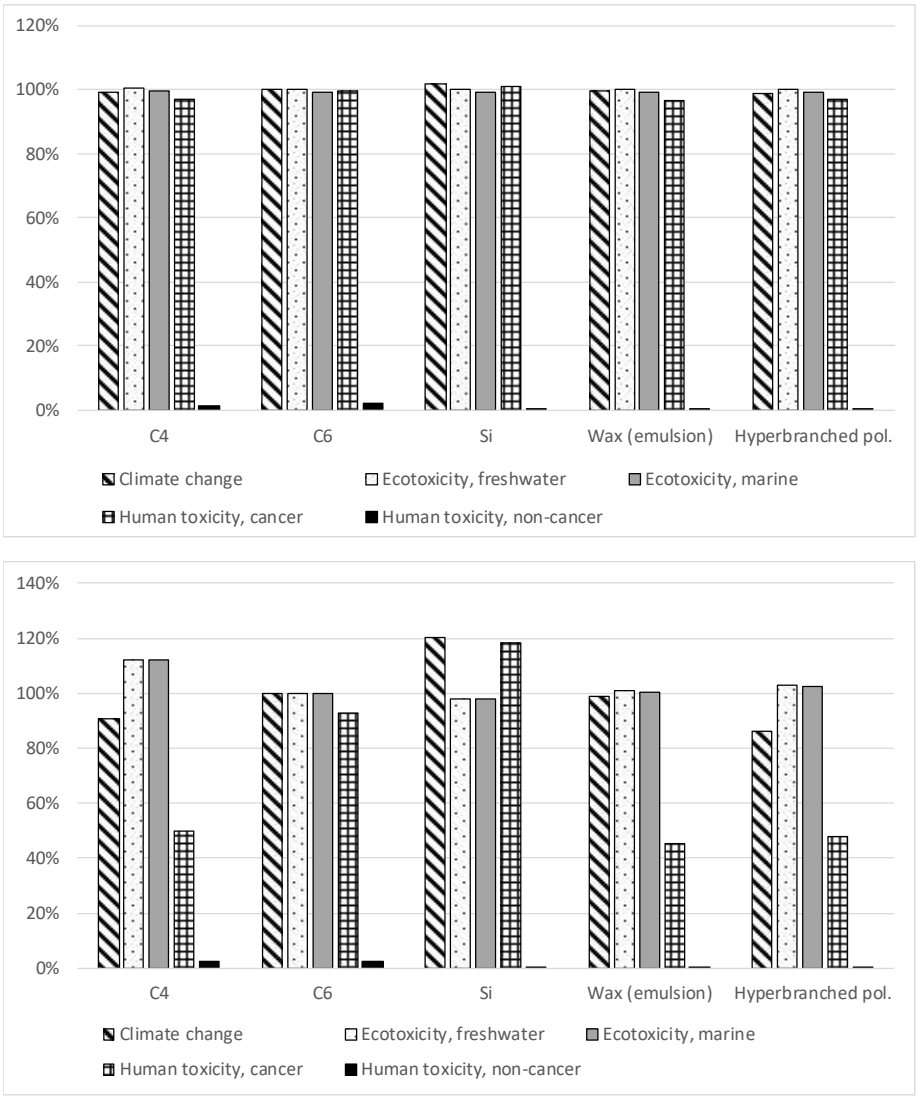

Figure 11: Indicator results of the DWR alternatives for climate change and (eco)toxicity normalised to indicator results of the benchmark, the C8 DWR. The upper panel shows the full garment life cycle results, while the lower panel shows results for the finishing only (textile excluded). 50% polymer degradation was assumed for the side-chain fluorinated polymers and effects factors roughly extrapolated from epidemiological data were used for the PFAAs. This is Figure 2 in Paper IV.

The LCA results in Paper IV expressed per functional unit could not differentiate between DWR alternatives beyond a differentiation between the fluorinated and non-fluorinated DWRs, as described above. This differentiation was dependent on the use of the CFs based on roughly extrapolated epidemiological data. As experimental data has shown that performance variation within each DWR category was as large as between categories (Schellenberger *et al.*, 2018) user scenarios and garment life lengths were not differentiated between the DWR systems. Scenario assessments (see Table 1 in Paper IV) were, instead, used to assess how changes in wash and re-impregnation frequencies and life length affected environmental performance (assessed with climate change and (eco)toxicity indicators). The life length of the garment was found to be a key parameter, independent of DWR system. The importance of the life length, in the human toxicity non-cancer indicator, was more pronounced for the wax and hyperbranched polymer based DWRs than for the side-chain fluorinated polymer and silicone- based DWRs. The higher potential toxicity of the DWR-related emissions of the fluorinated and silicone DWRs made re-impregnation relatively more important. Wash frequency was important for all DWR systems, except in the non-cancer toxicity indicator of the side-chain fluorinated polymer based DWRs (when CFs based on roughly extrapolated epidemiological data were used). The scenario assessments indicated that the optimal DWR from an environmental perspective would be a non-fluorinated DWR that imparts qualities to the garment that result in as few washes as possible and, most importantly, as long a life length as possible.

This cautious interpretation of the LCA results is a consequence of the high level of uncertainty in both estimated emissions and their potential impacts. Indicator results as shown in Figure 11 were calculated using all available CFs, not only the recommended CFs, *i.e.* also USEtox indicative CFs and non-MDQ CFs as presented in Papers II and III. As the hyperbranched polymer DWR system could not be specified to the same extent as the other DWR systems, their assessment is probably associated with additional uncertainty. While it was not possible to quantify the total uncertainty, it is likely that a difference between alternatives must be of several orders of magnitude to be relevant for (eco)toxicity indicators.

In summary, this thesis contributed to the answer to research question two by presenting hazard assessment and LCA results for five DWR types in relation to a C8 benchmark. It was found that all alternatives under study have improved environmental performance compared to the C8 DWRs. It was also found that non-fluorinated DWRs are clearly the preferred option for water repellency applications

(*i.e.* when oil repellency is not necessary) as there are indications that PFAA emissions from side-chain fluorinated polymer based DWR systems can have high potential for human health non-cancer toxicity.

3.3 What type of information would motivate consumers towards the substitution of hazardous PFASs found in outdoor garments?

Contrasting technical performance against user needs, as was done as part of the mapping of DWR alternatives (Paper I), illustrates the potential of consumer action to reduce risk from PFASs in DWR. A DWR provides multiple functions to a garment (*i.e.* not only water repellency but also repellency of other liquids and dirt), and the study in Paper I found that DWRs based on side-chain fluorinated polymers are readily substitutable (Figure 12) in the consumer segment, where the preferred function is comfort rather than hazard management, and water repellency provides sufficient function. Consumer action by choosing garments impregnated with non-fluorinated alternatives has the potential to be a relevant risk reduction measure.

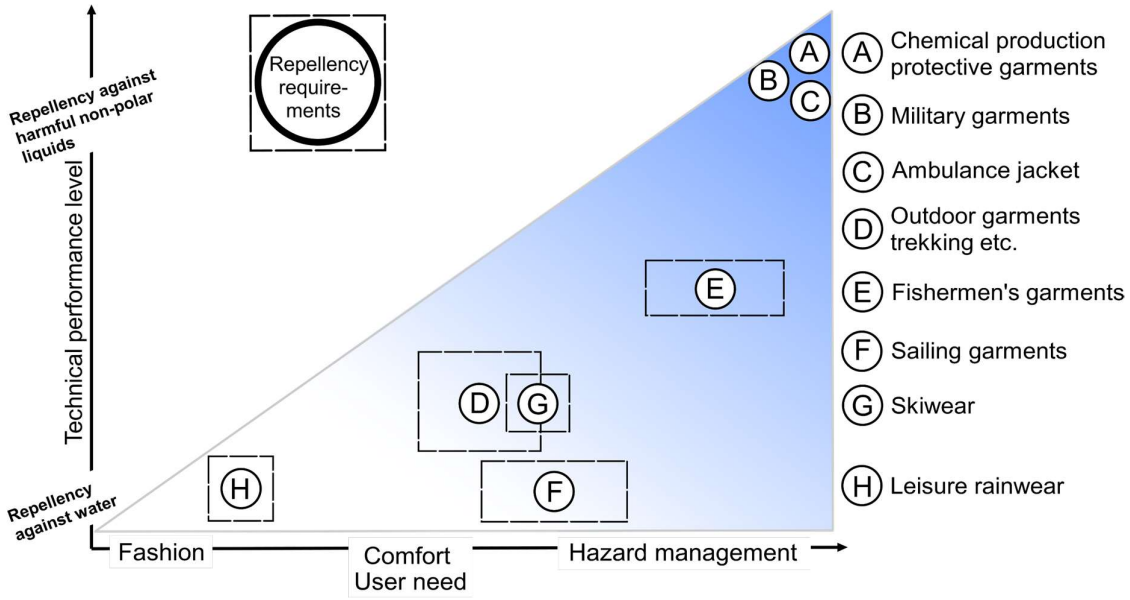

Figure 12: Illustration of the increased need for technical performance (in essence the degree of oil repellency and durability of oil and water repellency) with more advanced user needs; advancing from fashion to comfort to hazard management. Garment types (A–H) were subjectively placed in the graph. Additional work is needed to quantify the metrics on the graph's axes. This is Figure 3 in Paper I.

A panel of Swedes (part of the Gothenburg University Citizen Panel) were exposed to different types of information texts about hazardous fluorinated substances in the experiment in Paper VI (the survey experiment was conducted in June 2015, see Table 1 in Paper VI for information texts). They were asked to indicate their willingness-to-pay for a garment without such hazardous substances (also 'willingness-to-act' as the respondents were also asked if they would be willing to choose another

option at no price increase). The willingness-to-act/pay of this panel was high in the control group and in the four exposure groups that received information about hazardous fluorinated substances, Figure 13. The average was above 5 on a scale of 1-6 if the action was associated with no or a low (10%) price increase, and remained around 4 at a 50% price increase. Willingness-to-pay increased when information was given on the hazardousness of PFASs, and this effect was larger when the information was detailed and specific (*cf.* a description of PFASs as harmful to health with a description saying that PFASs are harmful to the unborn baby, are potential carcinogens and have the potential to cause reprotoxic effects). The effect of information was slightly higher when about environmental hazards compared to when it was about human health hazards. The effect of the information increased with an increase in price. The results of the survey showed that the Swedish public seem ready to substitute hazardous fluorinated chemicals in garments, but general information campaigns might not be effective as the willingness-to-pay/act is already high.

Awareness of the issue of fluorinated chemicals in garments and shoes was probably on the rise in Europe around the time of the survey described in Paper VI. Schellenberger *et al.* (2019a) did a consumer survey in July 2014 (respondents were contacted via social media with a focus on outdoor activities). 59% of 300 respondents claimed that they were unaware of concerns for the chemicals used for repellency in the outdoor industry. The Greenpeace Detox my Fashion campaign came to focus on PFAS use in the outdoor apparel sector in 2013 (Cousins *et al.*, 2019a), and the 2016 report, Leaving traces (Greenpeace, 2016), sparked public action leading to PFAS phase-outs by many market-leading brands (Cousins *et al.*, 2019a). Other NGO activities, *e.g.* by the Swedish Society for Nature Conservation or Chemsec, have raised the issue of PFAS hazardousness in parallel to Greenpeace actions. The respondents of the survey experiment (conducted in June 2015) in Paper VI could have been affected by the Greenpeace and other campaigns, which occurred in proximity in time to the survey experiment. Any new information campaign on PFAS hazards must carefully consider public prior knowledge about the subject, as this has been a topic for frequent media attention in recent years.

The effect of the information was a small, but statistically significant, increase in willingness-to-pay that was dependent on how the information was framed. This framing effect, *i.e.* how the hazard was described, was studied using regression analysis that controlled for perceived risk and environmental norms, as well as age, education, income, gender, and children, and the effect remained significant. The VBN-based model presented in Paper VI showed weak support for the theory that the effect of information framing was mediated by the 'degree of affection' (in this context: that of a

parent for their child) but could show a statistical significant interaction between the degree of affection and the perceived risk (*i.e.* the effect of the degree of affection was the highest for people who perceived environmental and human health risks as low). This model of willingness-to-pay as a response to information can be used in the design of targeted information campaigns or product labelling.

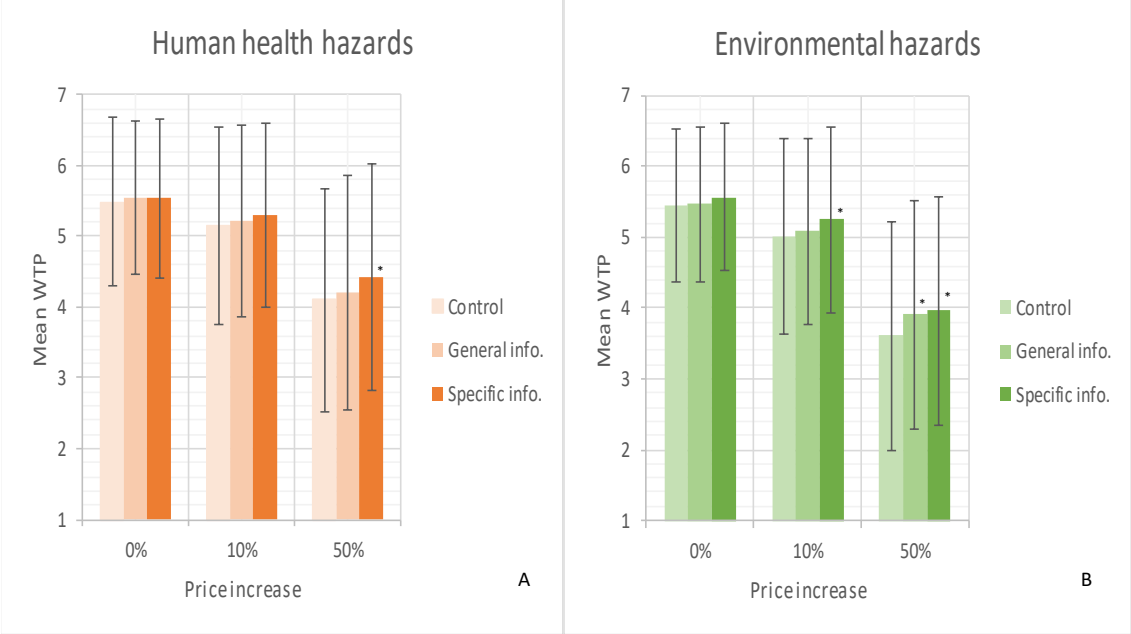

*Figure 13: Mean willingness-to-pay (WTP) for the children's overall (Scale 1-6), with no price increase, 10% and 50% price increase, when informed about hazards to human health (A, left panel) and hazards to the environment (B, right panel). Standard deviation in error bars. * denotes $p < 0.05$ in the comparison between control and experimental groups (Kruskal-Wallis 1-way ANOVA). This is Figure 2 in Paper VI.*

In summary, the research presented herein contributed to the answer to research question three by identifying the larger effect that more specific information about chemical hazards has on the willingness-to-pay for an alternative garment. Results also show that there are interactions between the risk perception of a person and the degree of affection for the object at risk, indicating possibilities for directed information campaigns.

4 Discussion

This discussion is focussed on implications for the application of a life cycle perspective in the case of substituting PFASs in DWRs. It is divided into four parts: i) how successful substitution of PFASs in DWRs can be achieved, ii) general concepts relevant for the application of LCA in CAA, iii) implications of the use of LCA for the inclusion of a life cycle perspective in CAA, and iv) proposals for a way forward.

4.1 Successful substitution of PFASs in DWRs

When the SUPFES project started in 2013, it was driven by the knowledge that DWRs give rise to emissions of hazardous long-chain PFAAs, such as PFOA. DWRs based on side-chain fluorinated polymers that are precursors to short-chain PFAAs were still considered viable alternatives. Since then, results as presented in this thesis, as well as the results of other research activities (see e.g. Cousins *et al.*, 2019c), have supported the conclusion that a complete phase-out of PFASs in DWRs is necessary. Temporary exceptions are relevant for essential uses, *e.g.* in medical textiles (Cousins *et al.*, 2019b). Results presented in Papers I, III, and IV show that all DWRs based on side-chain fluorinated polymers give rise to emissions of extremely persistent PFAAs with (eco)toxicity potential indicated to be far higher than that of chemicals associated with alternatives.

4.1.1 PFASs and the life cycle perspective

On the one hand, the PFASs studied in this thesis lend themselves well to the life cycle (eco)toxicity assessments included in this research. Conveniently for LCA, their persistence makes environmental accumulation key (*cf.* Paper III), and background exposures will become relatively more important than direct exposures for most people in the long term. The LCIA fate, exposure, and effect models, such as USEtox, that were used as a basis for the studies in Papers II-IV, where the focus was on indirect exposure, suffice to evaluate potential (eco)toxicity impacts. For other substances, life cycle (eco)toxicity considerations may require the use of models that also incorporate direct exposures, such as the near-field far-field model (Fantke *et al.*, 2016) that will be incorporated into a new version of USEtox (Fantke *et al.*, 2019). On the other hand, one is faced with the need to consider the implications of their extreme persistence when conducting a chemical substitution assessment of PFASs in DWR applications (Cousins *et al.*, 2019c).

Extreme persistence means that continuous emissions lead to increasing contamination, which is reflected by the high steady-state FFs calculated in the PFAA-adapted LCIA model (Paper III). Global PFAS use and the mobility of both PFAAs

and precursors mean that contamination will be difficult or impossible to reverse. This irreversible contamination makes knowledge gaps regarding PFAS effects particularly problematic. Risk reduction will be difficult if adverse effects, yet unknown to toxicology and therefore not captured in LCIA CFs, manifest (Cousins *et al.*, 2019c). With respect to PFASs, LCA results must be interpreted in conjunction with precautionary considerations due to the extreme persistence of terminal degradation products and their environmental performance implications.

A previous LCA has indicated that non-fluorinated DWR substitutes might not have an improved (eco)toxicity profile compared to side-chain fluorinated polymer based alternatives, from a life cycle perspective, due to the increased frequency of wash and care cycles (W. L. Gore & Associates GmbH, 2015). The results presented in Paper IV, however with appropriate precautionary considerations, indicate that PFAA emissions over the life cycle of a garment could contribute far more to (eco)toxicity indicator scores, in particular for non-cancer human toxicity, than other DWR-related emissions in both foreground and background systems. It is possible that the previous lack of appropriate CFs hindered the identification of this potential impact.

4.1.2 Public readiness for substitution and the relevant market response

In a consumer survey by Schellenberger *et al.* (2019a), fit, price, water resistance, and durability were identified as the most important factors for consumers when they purchase outdoor garments. Thus, consumers do not seem to request oil repellency specifically. Schellenberger *et al.* (2018) showed that non-fluorinated DWRs can have water repellency and durability that meet industry standards. The LCA results presented in Paper IV indicate that the anticipated problem-shifting of (eco)toxicity indicator results, from manufacturing to the use phase and due to an increase in the frequency of wash and care cycles (cf. W. L. Gore & Associates GmbH, 2015), does not outweigh the potential (eco)toxicity of PFASs. Hence, both consumer demands and environmental performance improvements should be possible to address in a substitution of side-chain fluorinated polymer based DWRs. The results of the survey experiment in Paper VI give a strong indication that the Swedish public is ready for a substitution to non-fluorinated DWRs. Results also indicate a potential for price increases, if necessary, for the alternative products, as the willingness-to-pay increased with detailed hazard information about PFASs. Garment and DWR manufacturers can find support in these findings when phasing out DWRs based on side-chain fluorinated polymers.

4.1.3 Selection criteria for DWR alternatives

Based on the results presented herein, the selection criteria for the alternative DWRs proposed are:

- Use non-fluorinated DWRs except in essential use applications, according to Cousins *et al.* (2019b).
- Select the DWR that can contribute to a long garment life-length, *e.g.* through DWR-durability and good stain repellency, thus reducing the need for re-impregnation and the frequency of wash and care cycles.
- Reduce the levels of impurities if silicone-based and side-chain fluorinated polymer based DWRs are used.

These recommendations are not product specific, which means that they can guide the garment manufacturer in a first step in selecting a DWR, however, additional test results on DWR performance in a specific application will be necessary for a final decision. In addition to these DWR specific considerations, a garment manufacturer can increase the environmental performance of a garment by means of energy and chemical emission considerations in fabric sourcing. Choosing a fabric with reduced fibre loss will decrease chemical emissions in the use phase (see Paper IV).

The LCA results presented in Paper IV indicate relative (eco)toxicity risks throughout the life cycle of a DWR-impregnated garment. The absolute acceptability of these risks has not been assessed, and it is up to the DWR manufacturers to ensure that the products they market are safe.

4.2 What can the LCA on DWRs tell us about the strengths and weaknesses of LCA as decision support in chemical substitution?

A theoretical strength of an LCA, *i.e.* its ability to quantitatively assess potential impacts in all relevant impact categories from a life cycle perspective, can at the same time potentially be its key weakness. In this section, experiences from the case study on application of LCA in the CAA on DWR alternatives in Paper IV will be used to identify and discuss a number of strengths and weaknesses of the use of LCA in CAA. It is acknowledged that the content and scope limitations of the case study also limit the scope of the discussion.

LCA is a **quantitative tool** making it possible, in principle, to directly compare two product systems with a seemingly straightforward answer; the product system with the lower LCIA result is the better option from an environmental perspective. However, uncertainties can be large. Few LCAs in the textile sector propagate uncertainties and variation for quantitative interpretation (Heimersson *et al.*, 2019, related work to this thesis, see p.V item D). That was the case for the LCA reported in Paper IV, for the simple reason that such meta-data were not available for many of the data sources. The use of LCA software was another limiting factor as meta-data were sometimes removed from the databases used for background data at implementation in the software. The approach chosen in Paper IV, as in many other LCA studies, was instead to evaluate different modelling options with the use of scenarios. Such scenario assessments, testing modelling choices (*cf.* Huijbregts, 1998a, b), are highly relevant in interpreting results but can also disguise the uncertainty of the results by giving the reader the impression that all uncertainties have been considered. The fact that LCA is a quantitative approach is not only a strength but also a potential weakness as it can be difficult to know what numerical differences between results are required for a robust ranking of alternatives.

LCA is intended to be **comprehensive;** all relevant environmental impacts are to be included (see *e.g.* ISO 14040). This is a major advantage of the method as it has the potential to reveal unexpected potential impacts. To do so, the LCI must include all flows relevant for all impact categories, however, that is seldom the case. Chemical flows relevant to toxicity were added to processes in DWR manufacturing in Paper IV, where such flows were known to exist, but these flows were not included in the database. Other flows, not in focus or not known, constituted data gaps. Current LCIA methods cover a broad range of impact categories, some more established and some still under development. Nevertheless, LCIA methods to date do not cover all relevant potential impacts. The research presented in this thesis contributes to efforts that make it possible to include potential (eco)toxicity impacts in an LCA, thus contributing to the comprehensiveness of the method. To some extent, the currently debated topic of plastic litter in the environment was addressed in the LCA (Paper IV) as fibre loss was quantified and converted into chemical emissions. Such expansions of the present method give the potential to increase the comprehensiveness of the method. Nevertheless, many relevant environmental problems remain to be captured with an LCIA. The strength of the comprehensive scope of an LCA, where many relevant impacts can be assessed together in a structured way, is also a potential weakness as stakeholders may mistakenly assume that all impacts have been considered.

LCA is a data-driven **learning** process about a system. This is an advantage, as it can create a knowledge transfer from the LCA modeller to stakeholders, such as producers of the product under study, or policy makers, as intended with the LCA in Paper IV. LCA work also has the potential to spread knowledge in a product's upstream value chain, through information to suppliers. In addition to LCA results, new knowledge can be generated by filling knowledge gaps as part of the LCA process. Remaining knowledge gaps can be filled to some extent by additional data searches, the use of estimated data, or the application of default values assigned to data gaps, *e.g.* by estimating emissions or propagating uncertainties when data for a substance is expected to be within the range of other substances for a specific parameter. These strategies were applied in the studies in Papers II and III. This base in knowledge, or facts, however, makes LCA difficult to combine with the precautionary principle in its execution. It is difficult to handle the highly uncertain prediction of potentially catastrophic effects. PFAAs can serve as an example. The data collection for the short-chain PFAAs in Paper III was done in a conservative (precautionary) way by extrapolating negative effects from PFOA to PFHxA and PFBS. This was possible as knowledge about the PFAAs is maturing, and low-level effects of PFOA have been found in several epidemiological studies (EFSA CONTAM Panel *et al.*, 2018, EFSA CONTAM Panel *et al.*, 20YY) and evidence is emerging of the equal toxic potency of PFAAs at equal internal concentrations (Gomis *et al.*, 2018, where the toxic potency concept was shown to be valid for liver effects). It is not possible to know if similar shifts in how PFAA carcinogenicity and ecotoxicity are assessed will happen in the future. The basis of LCA in existing knowledge is a strength as it enables learning, but it makes the method, in its current execution, hardly compatible with a precautionary approach, as precaution implies action before knowledge is complete.

LCA with its basis in **products and their function** makes possible alternative comparisons beyond 'drop in' substitute chemicals. This is an important feature of the method when moving towards 'fundamental substitution' (see 1.1.2). This potential was illustrated in the simple LCA case in Paper III, in which comparisons were made between surgical drapes with different physical designs. In the LCA in Paper IV, however, the scope did not exhaust these possibilities as comparisons were made only between DWR alternatives. The functional unit ('keeping dry and warm') would allow for the inclusion of other alternatives, such as plastic-coated textile garments with design interventions to promote ventilation. A broadened scope would require careful considerations as functionality differences might lead to limitations of possible user scenarios.

LCA offers the possibility to introduce life cycle considerations of chemical **(eco)toxicity potential impacts** in a CAA. The method does not replace a chemical risk assessment made to ensure safety, *e.g.* within a regulatory context such as a REACH registration, but offers a complementary assessment, with a product focus, relevant for risk management. In the LCA in Paper IV, (eco)toxicity potential impacts were compared between DWR systems to identify the environmentally preferable DWR. (Eco)toxicity potential impacts quantified for different parts of a garment's life cycle were also contrasted to identify relevant hot spots. Uncertainties limited the realisation of the full potential of this approach, but the results in Paper IV are nevertheless a relevant basis for recommendations. Potential pitfalls were identified in the review in Paper V in relation to the inclusion of chemical risk assessments in an LCA: bias resulting from model asymmetry, double counting, concealing relevant details, and inconsistent choice of parameter values. In a more traditional LCA approach, as in the LCA in Paper IV, the potential pitfalls are not identical to those identified for a study blending elements of risk assessment and LCA. However, model asymmetry is a possible result of the inevitable focus on the foreground system in data collection and the use of more specific data for this part of the system than for the background system. Furthermore, background and foreground processes can be inventoried according to different principles, which can lead to, *e.g.* data gaps with regards to emissions of chemicals (*cf.* 3.1).

Most importantly with regards to strengths, LCA is an established method for obtaining a **life cycle perspective**. There are numerous guidelines as well as ISO standards on how to conduct an LCA. There are also numerous experts globally with extensive experience of the LCA method. Considerable knowledge and data relevant to LCA collected to date have been incorporated into databases and software. This supply of methods, data, and competence provide one way to make life cycle considerations possible as part of a CAA, as exemplified by the case in Paper IV.

The strengths and weaknesses of LCA as a tool for identifying a preferable alternative in a CAA, identified in Papers IV and V, are summarised in Table 2.

Table 2: Summary of identified strengths and weaknesses of LCA as a tool for identifying preferable alternatives in a CAA, based on the case study of comparisons of DWR alternatives (Paper IV) and in the review of Paper V

LCA characteristic	Strength	Weakness
Quantitative	Easy to compare scores	Difficult to quantify uncertainties
Comprehensive	Chance to identify unexpected potential impacts	Risk of false security to have covered all relevant aspects
Data-driven learning	Promotes learning about the system	Incompatible with precautionary approaches
Product function basis	Allows for broad scopes, including fundamental or functional substitution	Very complex assessments
Inclusion of (eco)toxicity potential impacts	Possibility to evaluate potential (eco)toxicity impacts from a product perspective	Risk of model asymmetry
Life cycle perspective	Established method allows for broad implementation	Complexity of method introduces risk of erroneous use

4.3 Implications of the use of LCA for inclusion of a life cycle perspective in CAA

The research presented herein shows that LCA can provide relevant information for a chemical substitution assessment. In addition to the inclusion of impact categories other than (eco)toxicity, *e.g.* climate change and water scarcity, an LCA can also provide means to quantitatively compare potential (eco)toxicity impacts. Comparisons could be within a life cycle, *e.g.* foreground direct emissions compared to background energy-related emissions, or comparisons of aggregated (eco)toxicity indicator results (calculated for all emissions per functional unit) between product life cycles. Such (eco)toxicity LCA results are termed 'directional indicators' in CAA guidance (National Research Council, 2014), *i.e.* rough indicators on where (eco)toxicity impact hot spots can be expected and what emissions that contribute to those hot spots. Nevertheless, considerable effort is needed to achieve (eco)toxicity relevant LCIs and CFs for the LCA to generate relevant results, as is apparent in the findings in Papers II, III, and IV.

While there is a current movement in LCIA to increase the relevance of results with regionalised modelling (Wegener Sleeswijk, 2011, Verones *et al.*, 2017), the use of effect metrics close to actual exposure levels (Owsianiak *et al.*, 2019), and the inclusion of additional exposure pathways (Fantke *et al.*, 2019), there will always be a trade-off between the aim of capturing actual cause-effect chains and achieving robust comparisons, as long as comprehensive transport, fate and effect data are not available

for all chemicals. The design space proposed in Paper V is an illustration of such trade-offs, as it points out the dichotomy of possible approaches to assess cause-effect chains.

Experiences from the studies associated to the phase-out of PFASs from DWR applications (Papers I, III and IV), as described in this thesis, highlight a need to look at how (eco)toxicity indicators are constructed. It is time to reconnect to the dilemma in Section 3.1: how to know when additional data collection or model adaptions (*e.g.* of the LCIA model, as was done in Paper III) are needed. One important aspect in relation to this dilemma is that robust comparison is key in an LCIA, and, as pointed out by Udo de Haes *et al.* (2006), '…an equal approach for all chemicals to be included' is necessary. The current USEtox approach is, in theory, in line with an equal approach as it has specified procedures to calculate FFs, XFs, and EFs. The aim is to capture a chemical's behaviour, how it will partition and flow between different media, and the effects it will have, in a model world. Large differences in the availability of (eco)toxicity data and the effect endpoints studied for different chemicals, *e.g.* due to differing regulatory demands, however, make the calculation basis for the EFs heterogenous. The proposed data selection strategy in Paper II was intended to meet the demand for high-quality data that covers relevant endpoints, and the need to limit workload as an LCA covers many chemical flows, *i.e.* all possible data sources cannot be consulted for each chemical flow. This data collection strategy is an equal approach for all chemicals, but as it specifies data sources rather than data, and data availability differs among chemicals (see 2.2), this strategy is no guarantee for an equal assessment basis (the most relevant effect of each chemical is not necessarily found). It became necessary to expand data collection and modelling for PFASs, as done in the study in Paper III. Similar approaches may be needed for other chemicals, as highlighted for non-MDQ CFs in Paper II: 'In cases where MDQ CFs are needed, the recommendation to the LCA practitioner is to engage in interdisciplinary collaboration with experts in the field until additional data estimation methods and/or further guidance for their use is available'.

The prevailing (eco)toxicity approach in LCIA tries to capture the chemical emissions' actual effects, *i.e.* what happens once the chemical has been emitted. As apparent from the above, it is difficult to arrive at an equal assessment basis to make such comparisons relevant. Previous reasoning has also highlighted that the potential (eco)toxicity of extremely persistent chemicals may not be properly captured in an LCA until it is too late, as pollution cannot be reversed if discovered once it has gone global, and research and testing to find sensitive endpoints can take a long time. While a life cycle perspective is essential, CAA could benefit from the inclusion of complementary tools to LCA in its toolbox.

4.4 Proposal for a way forward based on case study experiences

LCA was used to provide a life cycle perspective for a holistic assessment of the case study that provided the basis of this thesis, a DWR alternative assessment. The LCA process was initiated early in the assessment to steer functionality and effects testing towards generating LCA-relevant data. The results of the LCA, however, were intended as one of the final outcomes of the CAA. Based on this case, where a complete and relevant (eco)toxicity LCIA assessment was found to be both resource intensive and uncertain, the inclusion of a life cycle perspective, and the evaluation of its results, are proposed to be conducted in a stepwise manner in chemical substitution assessments.

A life cycle perspective is proposed to be applied first in the identification or design of alternatives and second in a holistic assessment of alternatives that have been assessed as viable after primary life cycle considerations and hazard and functionality testing. The generic flow of a substitution process (Figure 3) is suggested to include life cycle considerations in both scoping and assessment steps (Figure 14). A functionality assessment can be made in several sequences with increased levels of testing, but this testing should not go beyond identifying basic functionality until a first screening of the potential problematic characteristics of alternatives has filtered out irrelevant options.

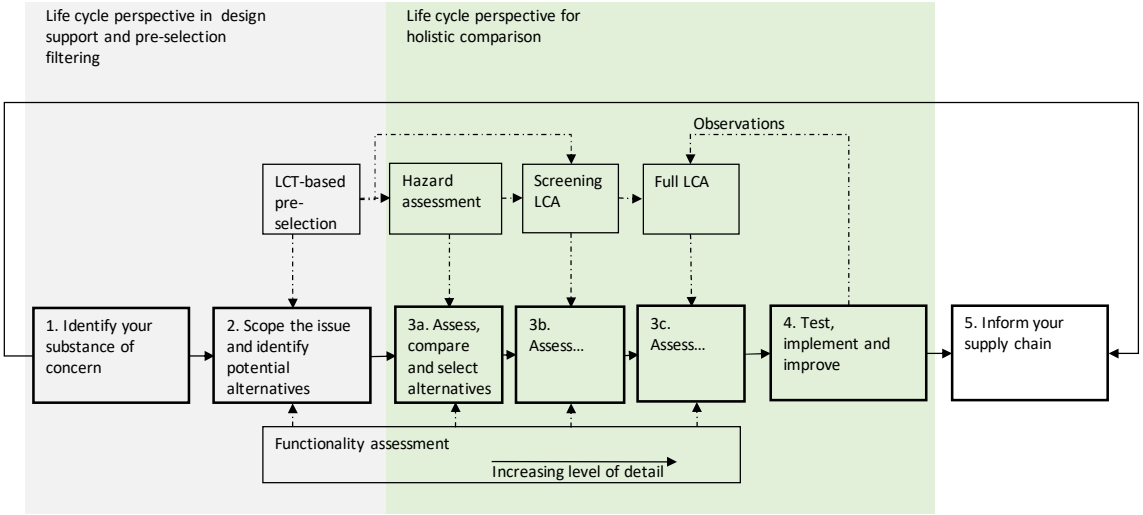

Figure 14: The chemical substitution process (the centre process flow, boxes 1-5, illustrate the generic substitution process from Figure 3). Possibilities to apply a life cycle perspective are indicated for steps 2 and 3. Solid arrows depict information flows about substances selected in the sub-steps. Dotted arrows depict information flows about substance/system characteristics obtained using the different assessment methods. The number of substances deemed as viable options are reduced between boxes 2 and 4, based on information obtained in the successively more detailed assessments. LCT=life cycle thinking.

The need for life cycle thinking early in the CAA process (e.g. the upper row of boxes in Figure 14) has already been brought forward in CAA frameworks, such as the California Department of Toxic Substances Control Alternatives Analysis Guide (DTSC, 2017). A detailed guidance on how to do so does not seem to be available (Tickner *et al.*, 2019a) but should typically be a staged process, as suggested in Figure 14. A product system mapping is the necessary starting point to identify potential for problem-shifting. Guidance for this assessment step must be comprehensive in impact coverage, yet simplified. For example, this could mean examining only the primary energy demand of a product or process for climate change without considering the type of energy source, as that step may require substantial additional data collection. For (eco)toxicity, this could mean focussing on a few priority hazard identifiers. It was found in this research that hazard identifiers in a pre-selection guidance should allow for a focus on extreme persistence alone (i.e. not necessarily in combination with high bioaccumulation potential or high toxicity) to make precautionary actions possible for substances such as the PFASs. The inclusion of degradation products is necessary. Given the diversity of the chemicals on the market, a single tool that is relevant for all chemical and product life cycles may not be possible. Roos and Peters (2015) have evaluated a textile wet-treatment process with methods for the semi-quantitative assessment of hazard and exposure and USEtox. Their findings deviated between methods and benchmarking (*i.e.* applying different methods to the same case study) was recommended to make assumptions explicit and to improve understanding of the results. Repositories of available tools and frameworks, such as the OECD Substitution and Alternatives Assessment Toolbox (OECD, 2020), facilitate the identification of the guidance to use in a specific case, however, further decision support would likely be helpful in many CAAs.

A life cycle thinking-based pre-selection procedure can be followed by more comprehensive hazard assessment and functionality testing for selected substances, and an LCA. The systems-understanding from the previous step provides a good basis for an LCA. A 'screening LCA' that applies data that are not specific to the product system but function as 'proxies', *e.g.* market averages or data from similar materials is a relevant first step. This screening LCA could be followed by a full LCA, if data are available that would make such an LCA meaningful. High throughput (eco)toxicity assessment tools could be valuable in these LCA steps. In cases when alternatives are new to the market, in particular, the LCA and product testing phase can benefit from being conducted in a circular manner, as in Figure 14, where test results on life length, expected use patterns, and emissions are fed into the LCA. This was done in the SUPFES project where LCA and functionality testing were conducted iteratively, and technical performance results were used in the LCA. The LCA should include

potential (eco)toxicity impacts in order to elucidate potential for problem-shifting within this impact category, thus avoiding a focus on energy-related impacts only.

5 Conclusions

To support the process of substituting hazardous PFASs in DWRs, the research contributions of this thesis were summarised in relation to three research questions (Chapter 3), thus generating three key messages:

- Calculating CFs for textile chemicals in general, and the PFAS degradation products PFAAs in particular, improves the relevance of LCA as decision support in the chemical substitution of the subset of PFASs in textile applications that are hazardous. This allows for otherwise unnoticed potential impacts to be captured.

- Alternative DWRs were indicated to differ substantially in (eco)toxicity performance compared to side-chain fluorinated polymer based C8 DWRs, and non-fluorinated DWRs have been found to be the environmentally most benign alternative, in both the hazard assessment and the life cycle assessment presented here.

- Consumers' motivation to purchase alternative products, for example outdoor garments in which environmentally friendly DWRs have been substituted for hazardous PFASs, can be raised by presenting detailed information about the hazards.

A holistic approach that includes life cycle perspective, *i.e.* by using LCA, was evaluated for its relevance in CAA (Chapter 4). While it can be argued that a life cycle perspective is imperative in the ethical management of chemical risks, LCA might need to be complemented with other tools or procedures to include a life cycle perspective in CAA. The research presented showed that an LCA can require extensive knowledge and resources if it is to provide relevant results for (eco)toxicity. Therefore, it seems reasonable to apply life cycle thinking in simpler model in CAA before the use of a more in-depth and detailed LCA. This would facilitate the identification of environmentally preferable alternatives in the early stages of a CAA.

6 Future research needs

The discussion of the research presented in this thesis has highlighted several uncertainties that can potentially be managed better after further research. To enhance the achievement of the two overall objectives of this thesis, certain kinds of additional data should be obtained in future research, particularly:

- The characteristics of new and non-fluorinated DWRs, such as their molecular structure, (eco)toxicity and relevant degradation products,
- Fate and exposure data for DWRs where such data are lacking,
- The link between DWR performance and garment performance, including the necessary frequency of wash and care cycles for different DWRs, and
- The strength of the link between the degree of motivation for consumer action which information about hazardous substances generates and the actual consumption behaviour in experiments with consumers in retail settings.

Additional improvements to LCIA (eco)toxicity models and the calculation of additional CFs will contribute to increase the relevance of LCA results for a CAA as well as other application areas. Two main research needs were identified in order to realise the methodological developments needed for the model proposed in Figure 14:

- Pre-selection guidance, based on life cycle thinking, should be further developed to support the inclusion of a life cycle perspective in CAA. Such guidance should be an attempt to operationalise sustainability targets, including but not limited to (eco)toxicity, from a life cycle perspective.
- To further increase the relevance of LCAs in the CAAs of textile and other products, improvements are needed to reduce the uncertainty of quantitative LCIA approaches. This means further improvements to data selection procedures and criteria to allow for the inclusion of all available data; and further improvement of data estimation methods. A reduction in uncertainty will facilitate the comparison of alternatives, thus improving the relevance of actions taken based on a CAA.

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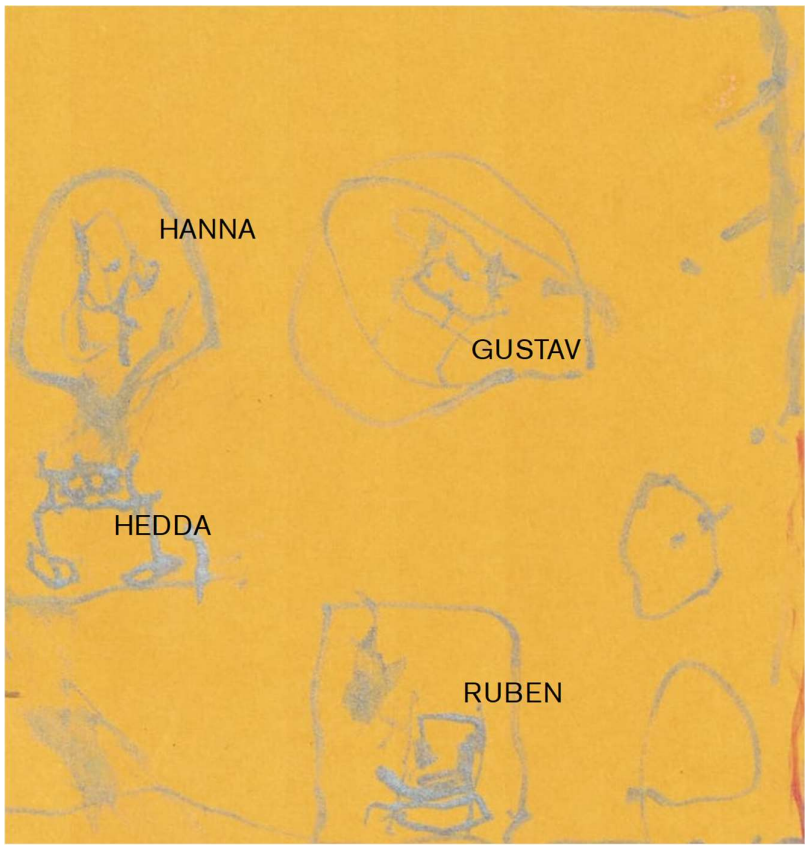

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